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Effect of Manganese on Co–Mn/CNT Bimetallic Catalyst Performance in Fischer–Tropsch Reaction

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Abstract: Cobalt (Co) catalyst is supported by carbon nanotubes (CNT) using a strong electrostatic adsorption (SEA) method. To promote activity and selectivity as well as find the optimum loading percentage and its effect on catalyst performance, manganese (Mn) has been added to the Co/CNT catalyst. Samples were characterized by a scanning electron microscope (SEM-EDX), transmission electron microscope (TEM), hydrogen temperature programmed reduction (H₂-TPR), Zeta potential, Brunauer–Emmett–Teller (BET) analysis, X-ray diffraction (XRD), and X-ray spectroscopy (XPS). TEM images illustrated an intake of metal particles which were highly dispersed, having a narrow particle size distribution of 6–8 nm to the external and internal CNT support. H₂-TPR showed a lower temperature reduction with Mn at 420 °C for Fischer–Tropsch synthesis (FTS) reaction. The Co–Mn/CNT catalyst performance test for FTS was performed at a temperature of 240 °C in a fixed-bed micro-reactor at a pressure of 2.0 MPa. The addition of manganese resulted in a lower methane selectivity and a higher C₅₊ product with an optimum percentage of 5% of manganese. CO conversion was 86.6% and had a C₅₊ selectivity of 81.5%, which was higher than the catalysts obtained using only Co on pretreated CNT.

Keywords: carbon nanotubes; thermal treatment; cobalt manganese; Fischer–Tropsch; catalyst; acid treatment

1. Introduction

The demand for energy is increasing every year in Europe and the United States, and the increase is dramatically faster in developing countries such as China, Brazil, and India (International Energy Agency, World Energy Outlook 2008). Sustainable energy production is a current world challenge that must remain environmentally friendly. Energy production technology with low CO₂ emission is promoted by various countries, especially in the European Union (EU). One of the promising technologies is the synthesis of fuels using Fischer–Tropsch (FT) technology [1]. Research and development work

is in progress to elevate the catalyst activity, selectivity, and stability of catalysts for FT reaction. The cobalt-based catalyst, in comparison to the iron-based catalyst, presents higher activity, selectivity, and stability with a lower water–gas shift reaction. The cobalt-based catalyst has a disadvantage on conventional support, such as silica and alumina, where it causes a high-temperature reduction, leading to sintering and decline of catalyst activation [2–4]. Using noble metals, such as ruthenium or platinum, as a promoter will decrease the cobalt catalyst temperature reduction [4–6]. Instead of conventional support, such as alumina and silica, employment of carbon nanotubes (CNT) provides support to help avoid using an expensive promoter to decrease the temperature reduction [7,8]. Promoters enhance the catalyst activity and are significantly important in order to have less methane selectivity and higher selectivity to C₅₊ hydrocarbons. Manganese as a promoter played this role and was examined in previous works. Keyser et al. and Colley et al. [9,10] reported MnO to coprecipitate on the cobalt catalyst as a promoter and resulted in higher olefin and lower methane selectivity. The same result was reported by Morales et al. [10,11] for MnO promoted Co on Titania, which resulted in higher activity and lower methane selectivity with the addition of manganese at 1 bar and temperature of 220 °C. A test was recorded for the impact of manganese promoter on non-oxidic and inert support [12,13]. Different carbon nanofibers (CNF)-supported manganese loading, adjusted by manganese nitrate re-infiltration tested on Co, were studied. In another study, Mn was examined by the same research group promoting cobalt on SiO₂ support and adding platinum as a promoter of reduction. Hence, the study examined the effect of adding Mn promoter to the Co/CNT catalyst performance.

2. Experimental

2.1. Purification and Functionalization of CNT Support

Prior to loading the metal catalyst to the CNT, functionalization and activation steps had to be conducted [14,15]. The aim of these steps was to enhance the interplay between the CNT support and the active catalyst sites. The functionalization and activation steps increased the purification of the CNT, resulting in the opening of the terminal caps of the tubular CNT and introducing the OH surface functionality over the CNT. From a reaction with concentrated nitric acid, the OH functional groups were found present on the surface of the CNT, which provide active sites for the attachment of the cobalt particles. Wet chemical oxidation is the most common method for functionalizing and activating the CNT [16,17]. Accordingly, 2 g of as-received CNT were charged into a single-necked, round-bottom flask with 35 vol% nitric acid. The solution was refluxed for 10 h at 110 °C. The mixture was cooled to ambient temperature at the end of the reflux, then diluted, filtered, and washed several times until the pH reached 7. For 12 h, the sample was dried at 120 °C. Subsequent to this acid treatment, the sample (CNT.A.) was subjected to a thermal treatment at 900 °C under argon flowing at 20 mL/min [18,19]. The synthesized acid and thermal-treated carbon nanotube support (CNT.A.T.) was subsequently used in the next step of this work.

2.2. The Point of Zero Charge, Co Impregnation on a Support, and Catalyst Preparation

The pH equilibrium at high oxide loading technique was implemented [20,21] to determine the CNT support point of zero loads (PZC). A series of solutions with a pH value ranging from 2 to 14 was created by adding nitric acid and ammonium hydroxide to distilled water. Accordingly, each 50 mL of the solution containing a specific pH reading (ranging from 2 to 14) was poured into a conical flask containing the pre-weighted CNT. All the mixtures in the series of various pH solutions were shaken for 1 h on a rotary shaker. A weighted amount of CNT was then added to a cobalt precursor solution with a pH of 14, where cobalt particles were adsorbed from an excess solution into the CNT support to prevent pH-value changes. Finally, the resulting CNT-supported catalyst was filtered and air dried for 24 h, followed by 400 °C calcination in a tubular furnace under an argon flow [22]. The strong electrostatic adsorption (SEA) method was used for catalyst synthesis, resulting in a well-dispersed Co nanoparticle on a low-co-charge CNT support [23,24].

2.3. Characterization

The physicochemical properties of the catalyst can significantly affect the catalyst's Fischer–Tropsch (FT) performance. A catalyst analysis of physical adsorption, temperature programmed hydrogen desorption (H_2 -TPD), and temperature programmed oxidation (TPO) was carried out using a Thermo Finnigan instrument (TPDRO 1100 MS, Waltham, MA, USA). A Zeiss LIBRA 200 FE TEM was used to conduct the transmission electron microscopy (TEM). A Bruker (A&S D8 Advanced Diffractometer, Singapore) instrument was used to analyze X-ray diffraction (XRD). In addition, the analysis of Fourier-transform infrared spectroscopy (FTIR), atomic absorption spectrometer (AAS), thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) total surface area analysis and total pore volume analysis were also carried out to further characterize the catalysts designed. Equations (1)–(4) were used to calculate reduction percentage based on the result derived from the temperature programmed reduction (TPR) figure peak area, dispersion percentage [25–27].

$$\% \text{ Reduction} = \frac{O_2 \text{ Uptake} \times \frac{2}{3} \times \text{Atomic Weight}}{\text{Percent Metal}} \quad (1)$$

In Equation (1), O_2 Uptake is the amount of O_2 in $\mu\text{mol/g.cat}$ calculated from TPO spectra of the catalyst, Atomic Weight is the molecular weight (MW) of the metal, and Percent Metal is the weight percentage of the metal in the catalyst.

$$\begin{aligned} \% \text{ Dispersion (total Co)} &= \frac{H_2 \text{ Uptake} \times \text{Atomic Weight} \times \text{Stoichiometry}}{\% \text{ Metal}} \\ &= \frac{\text{Number of Co Atoms on Surface}}{\text{Total Number of Co Atoms in Sample}} \times 100 \end{aligned} \quad (2)$$

In Equation (2), H_2 Uptake is the amount of H_2 consumed in mmol/g.cat calculated from the peak area of the H_2 -TPD spectra, Atomic Weight is the MW of the metal, % Metal is the weight percentage of the metal in the catalyst, and Stoichiometry is 2.

The number of active sites was calculated using Equation (3) [25].

$$\text{No. of active sites} = \frac{\text{Wt of Co in the Sample} \times \text{Reduction} \times \text{Dispersion} \times N_A}{\text{MW}} \quad (3)$$

where N_A is Avogadro's number and MW is the atomic weight of the metal.

$$H_2 \text{ uptake} \left(\frac{\text{moles}}{\text{gcat}} \right) = \frac{\text{Analytical Area from TPD} \times \text{Calibration Value}}{\text{Sample Weight} \times 24.5} \quad (4)$$

2.4. Microreactor Setup, Sampling, and Composition Analysis

Fischer–Tropsch synthesis was performed in a continuous flow fixed-bed reactor (PID Eng. & Tech, Micromeritics, GA 30093-2901, U.S.A.) equipped with mass flow controllers (Hi-Tec Bronkhorst, Ruurlo, The Netherlands). CO and H_2 (purity of 99.999%) were used as feed gases. The catalyst (0.02 g) was placed in a stainless-steel tube reactor (9 mm i.d. $\times$ 305 mm length) and sandwiched between quartz wool without further dilution. Prior to the reaction, the catalyst was reduced in situ under H_2 flow at 0.1 MPa and 420 °C for 10 h. The reaction was carried out in H_2 flowing at 50 mL min^{-1} and 25 mL min^{-1} of CO at 240 °C, 2.0 MPa and duration was varied from 10 to 130 h. The reactor was connected to an online gas chromatograph (Agilent 7890A, Hewlett-Packard Series 6890, Santa Clara, CA, U.S.A.) equipped with two thermal conductivity detector (TCD) detectors for analyzing hydrogen and permanent gases using Molsieve 13X and Hayesep Q columns, respectively. The hydrocarbons were detected using the flame ionization detector (FID) detector and a DB-1 column. All gas lines after the reactor were kept at 150 °C. Products were sampled at 30 min intervals and hydrocarbon selectivity was calculated at the end of the reaction (typically 10 h). Data were obtained at steady-state conditions with carbon balance of 95–102%. The reproducibility was ensured by repeating the experiments at least

twice under identical conditions and standard deviations of experimental results were found to be within $\pm 2.0\%$. Methane (CH_4) and C_{5+} selectivity were calculated via Equations (5)–(7), respectively, to calculate the gas product conversion for CO [25].

$$\text{CO conversion (\%)} = \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \times 100. \quad (5)$$

$$\text{CH}_4 \text{ selectivity (\%)} = \frac{\text{Mole of CH}_4}{\text{Total moles of hydrocarbons}} \times 100. \quad (6)$$

$$\text{C}_{5+} \text{ selectivity (\%)} = \frac{\text{Moles of C}_{5+}}{\text{Total moles of hydrocarbons}} \times 100. \quad (7)$$

To calculate the Fischer–Tropsch synthesis rate (RFTS) and water gas shift reaction rate (RWGS), Equations (8) and (9) were used for calculating the formation rate of the carbon dioxide (R FCO_2) respectively [2,28,29]:

$$\text{RFTS (g HC/g cat/h)} = \text{g hydrocarbons produced/g cat} \cdot \text{h}^{-1} \quad (8)$$

$$\text{RWGS (g CO}_2\text{/g cat/h)} = \text{RFCO}_2 = \text{g CO}_2 \text{ produced/g cat} \cdot \text{h}^{-1} \quad (9)$$

3. Results and Discussion

Figure 1a displays a plot of the final pH versus the initial pH of the solution for the determination of the PZC of the CNT. The plot shows a plateau and the PZC was identified at 9.5. To find an optimal pH value of a cobalt nitrate solution for the Co uptake in the CNT, the solution pH was adjusted within a range of 2–14, a weighted amount of CNT was added to each of the pre-determined pH solutions, and all the mixtures were shaken for 1 h. Figure 1b illustrates the Co uptake plot versus the pH solution from each sample prepared above, obtained from atomic absorption spectrophotometer (AAS) analysis. The optimum pH of the cobalt adsorption on the CNT support is also shown in Figure 1b [30,31].

Figure 1. (a) Point of zero charges (PZC) of the carbon nanotubes (CNT) support, (b) Co uptake versus the pH analyzed by atomic absorption spectroscopy (AAS).

A significant step before the catalytic performance reaction is the reduction and activation of the resulting calcined catalyst. The synthesized catalyst was activated at a rate of 1.8/h at 420 °C for 10 h in a fixed-bed micro-reactor under an H_2 flow rate of 20 mL/min. After activation (reduction) of the catalyst sample, the temperature under a helium gas flow was cooled to 240 °C. After in situ activations of the catalyst, the Fischer–Tropsch reaction was carried out at a ratio of 2/1 H_2/CO (v/v), 40 L/g-cat.h, 240 °C and 20 MPa.

3.1. Effect of Mn Loading on Catalyst Properties and Characterization

The influence of Mn loading has been investigated on the physicochemical properties of catalysts. To maximize the availability of active metal to catalyze the Fischer–Tropsch (FT) reaction, it is necessary to specify the optimal loading of Mn. The total metal loading of catalyst on CNT support was 10% and the addition of Mn as a catalyst promoter with 5%, 10%, 15% and 20% out of this 10% total metal loading. A series of Co–Mn/CNT catalysts were prepared with 0%, 5%, 10%, 15%, 20% of Mn loadings with the following sample coding, respectively: Co/CNT, 95Co5Mn/CNT, 90Co10Mn/CNT, 85Co15Mn/CNT, 80Co20Mn/CNT.

The TEM images of 95Co5Mn/CNT, 90Co10Mn/CNT, 85Co15Mn/CNT, 80Co20Mn/CNT catalysts revealed that the catalyst particles are well dispersed inside and outside the tubes, as shown in Figure 2. The measurement of particles size using TEM images of 150 catalyst particles was conducted. Catalyst oxide particles were synthesized with an optimum particle size of 6–8 nm, while the particles on the outer surface of CNT were up to 10 nm in particle size (Figure 2). CNT channels have limited particle growth within tubes [32]. A bar graph showing the size distribution of total particles inside and outside the CNT channels was dictated by the average particle size of the particle distribution collected from a collection of TEM images shown in Figure 3.

Figure 2. Transmission electron microscope (TEM) images of (a) 95Co5Mn/CNT, (b) 90Co10Mn/CNT, (c) 85Co15Mn/CNT, (d) 80Co20Mn/CNT catalysts.

Figure 3. Particle size distribution for 95Co5Mn/CNT catalyst.

The 95Co5Mn/CNT catalyst SEM image represents particles on the external CNT surface in Figure 5. SEM images reveal that nanotubes consist entirely of support material and no impurities such as carbon nanospheres.

Figure 4. Particle size distribution for 95Co5Mn/CNT catalyst.

Figure 4 displays a larger fraction (30%) of CNT-capsulated catalyst particles within 4 to 6 nm particle size range and increases the particle size range by 7 to 9 nm as a result of catalyst particle absorption on the CNT support surface [16].

Figure 5 displays SEM images of Co–Mn bimetallic catalyst with 5, 10, 15 and 20 percent of manganese. With increasing the Mn percentage from 5 to 20 percent agglomeration of catalyst, the active sites were increased. Increasing the agglomeration of catalyst particles led to declining catalytic activity and C₅₊ selectivity and is further discussed in Section 3.2. Agglomeration for 15 and 20 percent manganese is clearly visible in Figure 5c,d, respectively.

Figure 5. Scanning electron microscope (SEM) images of (a) 95Co5Mn/CNT, (b) 90Co10Mn/CNT, (c) 85Co15Mn/CNT, (d) 80Co20Mn/CNT catalysts.

As shown in Figure 6, the composition of the catalyst 95Co5Mn/CNT was studied using energy-dispersive X-ray spectrometry (EDX).

Figure 6. EDX spectra of 95Co5Mn/CNT.

Cobalt was provided at 0.770, 6.8 and 7.6 keV and manganese was shown at 0.705 and 6.1 keV, respectively. According to Kozhuharova et al. [33], the peak at 6.8 keV can also be linked to the metal stage comprising both cobalt and manganese metals.

Table 1 presents the textural properties results of the BET surface area and total pore volume. Results show the increase in total area (BET) from 217.5 to 225.3 m²/g with a 5 to 20 wt percent increase in Mn load. Surface area growth may be due to higher nanoparticles dispersion.

Table 1. Textural properties of Co/CNT catalysts at various wt% loading.

Samples	BET Surface Area (m ² /g)	Total Pore Volume (m ³ /g)
Pristine CNT	138.2	1.58
CNT.A	223.2	0.88
CNT.A.T	266.4	0.54
95Co5Mn/CNT.A.T	217.5	0.36
90Co10Mn/CNT.A.T	220.8	0.48
85Co15Mn/CNT.A.T	223.4	0.55
80Co20Mn/CNT.A.T	225.3	0.58

The results show that with increasing Mn percent of catalysts from 5% to 20%, the total pore volume increased from 0.36 to 0.58 (m³/g) respectively. The lower total pore volume of catalysts 80Co20Mn/CNT.A.T compared to CNT.A indicates that, due to loading on support by Co and Mn, some pore blockage occurred. Incorporating cobalt and manganese into CNT support resulted in an increase of total pore volumes in both BET surface areas.

Figure 7 displays the XRD patterns of CNT support and catalyst samples. The 26° and 44° peaks correspond to nanotubes of carbon [34]. The monometallic Co/CNT sample shows Co₃O₄ spinel diffraction lines at two ranges of 32° and 37.1° [34], while monometallic Mn/CNT displays diffraction lines. The A.T sample shows a hematite pattern (Mn₂O₃) at two values of 32.5° and 44° [35]. In bimetallic 95Co5Mn/CNT catalyst XRD patterns, Co₃O₄ spinel diffraction lines appear at approximately 32.5° and 37.1°. For the catalyst, however, Mn₂O₃ was correlated with only a small peak at 44° due to low manganese content.

Figure 7. XRD spectra of (a) CNT (b) Co/CNT.A.T (c) Mn/CNT.A.T (d) 95Co5Mn/CNT.A.T catalysts.

XRD patterns with different Mn metal loads of calcined catalysts are shown in Figure 8. In CNT's XRD pattern and all catalysts, peaks at 25° and 43° are connected with carbon nanotubes, while peaks in the catalyst are linked with distinct Co₃O₄ crystal planes [36]. The most prominent peak was observed at 36.8° for Co₃O₄. Because of the low number of Mn promoters in the catalyst XRD pattern, lower intensity peaks are observed at 32.5° and 44°, indicating Mn oxide diffraction lines (Figure 8). Table 2 shows the average particle size of the catalysts calculated from XRD and TEM images [37]. From Table 2, the average particle size of Co₃O₄ decreases from 7.5 to 6.5 when manganese load increases from 5% to 20%, a similar trend to the results of the TEM analysis (Figure 2). Cobalt average particle size increases due to the agglomeration of cobalt particles. Table 2 shows that by adding Mn to the Co catalyst, the average particle size decreases slightly.

Table 2. XRD and TEM results for Co–Mn bimetallic catalysts.

Catalyst	XRD ($d_{\text{Co}_3\text{O}_4}$) (nm)	TEM Ave. Size (nm)
95Co5Mn/CNT.A.T	7.5	7.7
90Co10Mn/CNT.A.T	7.2	7.3
85Co15Mn/CNT.A.T	6.8	6.9
80Co20Mn/CNT.A.T	6.5	6.7

Figure 8. XRD profile of Co–Mn/CNT with Mn content (a) 5, (b) 10, (c) 15 and (d) 20%.

The H_2 -TPR profiles of CNT support and calcined monometallic catalysts (Co/CNT and Mn/CNT) are shown in Figure 9.

Figure 9. Hydrogen temperature programmed reduction (H_2 -TPR) profiles of (a) CNT, (b) 10Co/CNT (c) 10Mn/CNT.

The first peak of the monometallic cobalt catalyst TPR profile was allocated to the reduction of Co_3O_4 to CoO , while the second peak, with a wide shoulder, was primarily allocated to the second reduction step, which is a reduction of CoO to Co^0 [34]. The second peak also involves reducing the number of cobalt active sites that interact with support, expanding the H_2 -TPR peaks to higher temperatures [38]. Figure 9 shows the first reduction peak of Co/CNT at 220 °C and the second reduction peak of 420 °C. As illustrated by H_2 -TPR of pure CNT support at 600 °C, CNT support gasification was

assigned to the small peak at about 593 °C at the H₂-TPR profile of the 10Co/CNT catalyst. The first H₂-TPR peak ranged from 360 °C to 370 °C, while the second H₂-TPR peak ranged from 600 °C to 620 °C [39]. Figure 9 indicated that in the case of Co/CNT, both reduction peaks are shifted to lower temperatures, performing an easier reduction process. As a result, the first H₂-TPR peak temperature drops by 100–120 °C, while the second H₂-TPR peak temperature drops by 180–200 °C. The results indicate that the reduction temperature of hard-to-reduce catalyst active sites (450–650 °C) decreased because of a lower degree of interaction between the support of Co and CNT due to the use of CNT as cobalt catalyst support [34].

H₂-TPR of monometallic Mn/CNT catalyst is complex and exhibits two broad peaks at 290 and 430 °C. The following consecutive reduction steps can be assigned to the first peaks: Mn₂O₃ → Mn₃O₄ → MnO [40]. As designated by H₂-TPR of pure CNT support and monometallic cobalt catalyst, the third peak in the Mn/CNT catalyst H₂-TPR spectra was due to support gasification. Cobalt and manganese loading on CNT appears to decrease CNT gasification temperature. It is noted that the relative Mn/CNT catalyst intake of hydrogen is lower than the catalyst of Co/CNT (Figure 9). O'Shea et al. [41] studied the TPR of the manganese catalyst (10 wt%) supported by silica. They showed that the first and second H₂-TPR peak temperatures for the Mn/SiO₂ catalyst were 371 and 520 °C, respectively. Comparison of H₂-TPR results of Mn/CNT catalyst were reported by O'Shea et al. Figure 10 demonstrates the outcomes of chemisorption of the sample and demonstrates that the addition of tiny quantities of Mn to the cobalt catalyst moved both H₂-TPR peaks to lower temperatures [41]. The 10 wt% Mn to Co catalyst caused the first H₂-TPR peak to decline from 330 to 290 °C and the second H₂-TPR peak to decline from 500 to 450 °C. The findings also show that the second H₂-TPR peak tailing has become considerably wider by adding 15 and 20 wt% of manganese to the cobalt catalyst, resulting in a challenging reduction method for cobalt oxides. There is a chance that a decrease could be ascribed in a Co–Mn mixed oxide stage to the broad tailing peak. It should be noted that the wide tailing of the second H₂-TPR peak severely overshadows the peak indicating CNT gasification [36].

Figure 10. H₂-TPR profiles of catalysts (a) CNT.A.T, (b) 95Co5Mn/CNT, (c) 90Co10Mn/CNT, (d) 85Co15Mn/CNT, (e) 80Co20Mn/CNT.

Table 3 illustrates the results of the chemisorption samples. Adding 5 wt% to 20 wt% of Mn to Co catalysts led to a significant improvement in the reducibility of catalysts. Increasing Mn loading to 10 wt% led only to a marginal effect on the reducibility of catalysts. Manganese increases the reducibility of both Co₃O₄ and Co-oxide active sites as shown by percentage reduction (Table 3 and Figure 10). The first peak reducibility is increased more than the second peak, as shown in Figure 10. Das et al. demonstrated that Mn oxide reduction occurs below cobalt temperatures. They concluded that reducing Mn increases the reduction of cobalt oxide from Mn to cobalt oxide by spillover hydrogen. Mn may also improve the reduction with CNT support of smaller, strongly interacting cobalt [42].

Table 3 shows the results of the Co–Mn/CNT catalysts desorption programmed hydrogen temperature (H_2 -TPR).

Table 3. H_2 chemisorption results.

Samples	1st Peak °C	2nd Peak °C	H_2 Uptake *	% Disp.	Reduction (%)	No of Active Sites $\times (10^{20})$
CNT.A.T	—	590	—	—	—	—
Co/CNT	279	508	100.0	14.7	50.1	3.5
95Co5Mn/CNT.A.T	258	502	100.1	22.1	68.1	5.8
90Co10Mn/CNT.A.T	251	494	97.5	20.3	63.8	5.1
85Co15Mn/CNT.A.T	245	487	94.3	18.4	55.2	4.6
80Co20Mn/CNT.A.T	232	478	91.6	17.1	48.8	4.2
Mn/CNT	269	481	32.4	12.2	35.7	3.1

* H_2 uptake: (μ mole H_2 desorbed/g cat.) for 10% total metal loading on support.

Table 3 shows that by adding 5 wt% manganese to Co/CNT monometallic catalyst, hydrogen uptake slightly increased and dispersion percentage increased from 14.7 to 22.1. Co particle sizes, however, had reduced Mn by adding to the catalyst and attributed to reducing smaller cobalt crystallites when Mn promotes catalysts. Comparison of the data in Table 3 for the reduction percentage of the Co/CNT catalyst (0.51) with previous studies [39] on Co/ γ - Al_2O_3 catalysts (reduction percentage between 19 and 23) shows that the use of CNT as support for cobalt catalysts significantly increased the reduction percentage and was due to a lower degree of Co–CNT interaction [34], and increased availability of active metal catalyst reaction atoms in CNT-supported catalysts compared to catalysts Co/ γ - Al_2O_3 [39]. A small amount of Mn (5%) enhanced reducibility of bimetallic catalyst and higher concentration percentage of Mn (i.e., Mn > 10 wt%) resulted in a decrease in the reduction percentage [41]. Table 3 shows that for the Co/CNT catalyst, the amount of H_2 intake was higher than that of the Mn/CNT catalyst and for bimetallic catalysts with increased Mn content, increased H_2 intake passed through a maximum 5 wt% Mn load and then decreased. The data suggest that the surface was affected by the Mn and Co mixture at a higher Mn loading. Unlike H_2 uptake and reduction percentage, the percentage of Mn/CNT dispersion was lower than the catalyst for Co/CNT. With the addition of Mn, the percentage of dispersion increased significantly (22.1%) for bimetallic catalysts, passing through a 5 wt% maximum at Mn load. Then the percentage dropped (Table 3). It thus appears that the Mn–Co ratio plays a key role in controlling metal dispersion and bimetallic system reduction. The X-ray photoelectron spectroscopy (XPS) method was researched to know the impact of Mn in Co catalyst on the chemical nature, surface structure, oxidation status, and type of interaction with Co–Mn.

Figure 11 demonstrates sample XPS spectra and Table 4 summarizes the results. Figure 11 shows the Co/CNT catalyst XPS spectra and shows peaks of $Co2p_{3/2}$ and $Co2p_{1/2}$ at 781.6 eV and 797.1 eV binding energy (BE), respectively. Split in binding energy ΔE_{Co} between $Co2p_{1/2}$ – $Co2p_{3/2}$ was 16.0 eV and satellite peak at +6 eV from $Co2p_{3/2}$ were observed. As shown in Figure 11, the $Co2p_{3/2}$ peak also consisted of a double, Co^{3+} (octahedral environment) at BE = 789.4 eV and Co^{2+} (tetrahedral environment) at BE = 788.3–788.6 eV was characteristic of Co_3O_4 peaks [41,43–45]. For bimetallic catalysts, it was found that $Co2p$ binding energies had shifted to a lower value having nearly the same ΔE_{Co} . However, determination of Co cations in bimetallic systems is difficult, as similar spectra can be obtained for CoO , Co_3O_4 and Co_2O_3 oxides. In bimetallic Co systems, values of ΔE_{Co} and relative populations of Co^{2+}/Co^{3+} cations provide important information regarding Co cations. When the peak is approximately 6 eV from the Co-main peak, it indicates that Co is in Co^{2+} oxidation state with ΔE_{Co} values between 9–10 eV indicating the presence of Co^{3+} species. Based on observations, it could be concluded that Co^{2+} and Co^{3+} existed both in monometallic and bimetallic nanocatalysts. The only difference was that Co^{2+} was predominantly present in the monometallic system while in bimetallic systems the relative population of Co^{2+} increased. As shown in Table 4, with the incorporation of Mn into Co catalysts, the ratio of Co^{2+}/Co^{3+} increases. The highest ratio of Co^{2+}/Co^{3+} was observed for bimetallic combination with 95Co5Mn/CNT formulation. It implies that the interaction of Co–Mn

was strengthened with an increase in the amount of Mn incorporated as Mn(IV) ions constrained electrooxidation of Co^{2+} to higher oxidation states [46]. The shift in Co2p binding energies to higher BE values and increase in $\text{Co}^{2+}/\text{Co}^{3+}$ populations indicated an electronic modification of Co species where an electronic transfer could have occurred between Co and Mn species and attributed to the near distance interaction between Co and Mn which had resulted in the formation of alloy. Surface atomic ratios of Co/Mn were calculated from XPS analysis. Results shown for the bimetallic formulation; the surface atomic ratios of Co/Mn increased as Mn was greater than 5 wt%. The decrease in $\text{Co}^{3+}/\text{Mn}^{4+}$ atomic ratios could presumably be due to partial coverage of Co atoms with Mn as more Mn atoms were present on the surface of the catalyst.

Figure 11. XPS Co2p spectra of Co/CNT.

The Mn2p spectrum is shown in Figure 12. For the bimetallic Mn nanocatalyst, binding energies at 653.6 eV and 641.7 eV were assigned to $\text{Mn}2\text{p}_{1/2}$ and $\text{Mn}2\text{p}_{3/2}$, respectively. Results indicated that Mn was present in the Mn(IV) oxidation state [47]. There was no significant difference in monometallic and bimetallic spectra, but BE values were shifted to higher energies, indicating an electronic modification in the bimetallic catalyst. It can be concluded from XPS analysis that in monometallic Co and Mn, Co and Mn were present in Co_3O_4 and MnO_2 phases, respectively. Incorporation of Mn into Co had resulted in an electronic modification where an increase in $\text{Co}^{2+}/\text{Co}^{3+}$ ratio was detected.

Table 4. XPS analysis of catalysts.

Catalyst	XPS BE (eV)				Atomic Ratios		ΔE_{Co}
	Co2p _{3/2}	Co2p _{1/2}	Mn2p _{3/2}	Mn2p _{1/2}	Co ³⁺ /Mn ⁴⁺	Co ²⁺ /Co ³⁺	
Co/CNT	780.5	796.0	—	—	—	0.19	15.5
5Mn95Co/CNT	780.2	795.3	641.4	652.9	2.6	1.33	15.1
10Mn90Co/CNT	780.7	796.4	641.6	653.3	2.01	0.72	15.7
15Mn85Co/CNT	781.0	796.9	641.5	653.2	1.7	0.89	15.9
20Mn80Co/CNT	781.2	797.3	641.6	654.1	1.1	0.93	16.1
Mn/CNT	—	—	641.9	653.6	—	—	11.9

$$\Delta E_{\text{Co}} = \text{Co}2\text{p}_{1/2} - \text{Co}2\text{p}_{3/2}.$$

Figure 12. XPS Mn2p spectra of 95Co5Mn/CNT.

3.2. Effect of Mn Promoter on Catalyst Performance

Prior to reaction, reduction and activation of calcined catalysts are important steps [48]. Catalysts were activated with the flow of H_2 , 1.8 L/h at 420 °C for 12.5 h. After activation of the in situ catalyst, the temperature of the reaction was cooled to the desired reaction temperature and flushed with helium for 10 min. The Fischer–Tropsch reaction test was performed at 2/1 H_2/CO (v/v), 40 L/g-cat/h, 240 °C and 20 atm pressure. Figure 13 indicates the proportion of CO conversion, FTS and WGS reaction rates promoted for the Co10 catalyst with different proportions of Mn.

Figure 13. Percentage of CO conversion, Fischer–Tropsch synthesis (FTS) rate (g HC/g cat/h) and WGS rate (g CO₂/g cat/h) for different catalyst formulation on CNT support.

Figure 13 shows that the percentage of the catalyst's CO conversion and FTS rate increased with increasing Mn from 5% to 10% and increasing Mn% from 10% to 20% led to a decrease for CO conversion and FTS rate. The trend for CO conversion and FTS rate is similar to that for hydrogen

intake compared to Figure 13 and H₂ chemisorption information from Table 3. Figure 13 indicates hydrogen uptake, CO conversion rate, FTS rate, and WGS rate rises. In addition, the incorporation of Mn in the cobalt catalyst improved the decrease proportion as well as the absorption of H₂, which increased the accessible cobalt surface atoms and active site for FTS and WGS reactions. Results showed that catalyst FT activity is strongly dependent on the decreased cobalt locations of the surface (Figure 13). Figure 13 shows the reduction of manganese oxide at temperatures below the reduction of cobalt. Reduced Mn increases the reduction of cobalt oxides as the spillover of hydrogen from Mn to cobalt oxide and manganese may increase the reduction of lower-size cobalt active sites which, in the case of the unpromoted catalyst, may not be reduced. Thus, in Mn-promoted catalysts, Mn increases the number of active surface Co sites available for FT reaction and thus increases the percentage of CO conversion and FTS reaction rate. The addition of Mn promoter to cobalt catalysts is believed to change the morphology of the catalyst. Mn has been reported to be mostly enriched on the cobalt surface [49]. Considering Mn's higher cobalt FTS activity and its cobalt surface, enrichment may be another cause of catalyst activity improvement promoted by Mn. The benefits of adding Mn, however, are not limited to enhancing reducibility and activity of the cobalt catalyst supported by CNT. It should be noted that many researchers are investigating the effect of Mn on cobalt catalyst activity supported on oxide supports [50]. It has been demonstrated that adding 5 wt% of Mn to the Co/CNT catalyst increase the percentage of CO conversion from 58.7% to 86.6% [29]. Due to the promotion of Mn catalysts, the variation in percentage CO conversion increase achieved with CNT support can be related to improvements in the percentage of reduced cobalt. It is easier to reduce cobalt active sites on CNT-supported catalysts than to reduce cobalt particles supported by oxide.

Figure 13 also illustrates that with the addition of Mn to Co 10% catalyst, the WGS reaction rate decreases. The decrease in the rate of WGS reaction may be corresponded to the decrease in partial water pressure due to a decrease in the rate of FTS reaction. Table 5 presents the effects on CH₄, C₂–C₄ and C₅₊ products of Mn promoter on FTS selectivity. It clearly shows a reduction in the selectivity of methane and C₂–C₄ light gaseous products, and an increase in the selectivity of C₅₊ hydrocarbons by promoting 5 wt% Mn cobalt catalysts. Manganese increases the selectivity of C₅₊ and shows lower selectivity of 5 wt% to methane, the catalyst promoted by Mn. Increasing the Mn from 5% to 20% of hydrocarbons monotonically decreases selectivity to higher molecular weight. Table 5 presents the chain growth probability (α) of FTS products for monometallic and bimetallic catalysts. By increasing the amount of Mn promoter, a shift to higher molecular weight hydrocarbons is evident from the rising trend in chain growth probability. In molecular weight hydrocarbons, Mn is more selective than cobalt. The increase in C₅₊ selectivity, relative to the unpromoted catalyst, could be due to Mn enrichment for Co–Mn bimetallic catalysts on the cobalt crystallite surface. Increasing CO uptake decreases the mobility of H₂ on the catalyst surface, leading to reduced CO conversion rates of FTS and WGS [51]. It should be observed that measurements were taken for C₂–C₇ hydrocarbon α -olefin/n-paraffin ratios. Table 5 demonstrates that the alkali-promoted cobalt catalyst has considerably enhanced α -olefin selectivity. Regarded as main FTS products, 1-alkenes maybe hydrogenated to alkanes or isomerized to 2-alkenes during the reaction. An alkali promoter appears to reduce subsequent reactions drastically. Studies of alkali-promoted CO chemisorption catalysts (Table 5) show that the mobility of hydrogen by blocking low-coordination edge and corner sites for dissociative hydrogen adsorption was significantly restricted to alkali promotion.

The rise in CO adsorption levels, as well as the reduction in hydrogen adsorption levels, could explain the reduction in 1-alkene hydrogenation to alkanes qualitatively, leading to enhanced α -olefin/n-paraffin ratios. Table 5 results also indicate that bimetallic Co–Mn catalysts result in lower methane selectivity while improving selectivity to greater molecular weight hydrocarbons. The decrease in methane selectivity can be explained on the catalyst surface based on partial hydrogen atom pressure (Table 5), which resulted in a decrease in paraffin (i.e., methane) rate during the FTS reaction. The enhanced selectivity of cobalt catalyst hydrocarbons of greater molecular weight following alkali promotion may be explained by the enhanced concentration of α -olefin and the

re-adsorption and chain initiation of main use products on the catalyst surface resulting in the ultimate desorption of α -olefins as larger products [52]. The Co/CNT catalyst showed 58.7% CO conversion for monometallic catalysts compared to the Mn/CNT catalyst with 23.8 percent CO conversion. As shown in Figure 13, with the addition of 5 wt% Mn loading to the cobalt catalyst, the percentage of CO conversion was boosted. However once Mn loading increasing from 10% to 20% the CO conversion decreased. Table 5 shows that adding a small amount of manganese (i.e., 5 wt%) to a cobalt catalyst resulted in higher percentage reduction and catalyst active site dispersion. Improvements in metal dispersion and reduction create more active metal atoms accessible for FTS reaction, considerably improving catalyst activity. Increasing the quantity of Mn above 5% will reduce the proportion of dispersion, resulting in a reduced proportion of CO conversion. A reduction in CO conversion on the surface of bimetallic catalysts could be ascribed to Mn enrichment. Figure 13 shows that the FTS reaction rate increases by adding manganese to the cobalt catalyst, which synthesized with a maximum of 5 wt% at Mn loading. The same behavior had been observed by O'Shea et al., promoting cobalt catalyst with adding Mn from 5 wt% to 20 wt% [41]. The 95Co5Mn/CNT catalyst sample increased the FTS rate by 0.36%, while 10 wt% and 20 wt% added manganese percentages dropped FTS by 0.29% and 0.19%, respectively. Figure 13 also shows that by adding manganese to the cobalt catalyst, the WGS reaction rate has been reduced. The WGS reaction rate at low Mn values (i.e., 5 wt% of Mn) was not significantly reduced. Adding higher amount of Mn up to 20 wt% to Co/CNT catalyst led to WGS rate dropped significantly. Figure 13 shows that the WGS rate followed FTS and was consumed in the WGS reaction corresponding to the H_2O produced by FTS at a low Mn content value (95Co5Mn/CNT). Figure 13 shown for Mn loading catalysts higher than 5 wt%, the percentage of the WGS reaction rate is lower than the FTS rate. The lower WGS reaction rate could be due to the lower CO dissociative absorption capacity of manganese catalysts. Distributions of catalyst products are shown in Table 5.

Table 5. Product selectivity for mono and bimetallic catalysts.

Catalyst	%CO _{Con}	CH ₄ %	(C ₂ –C ₄)%	C ₅₊ %	Yield%	CO ₂ %	O/P	α
Co/CNT	58.7	9.5	13.4	59.1	34.7	10.4	0.60	0.591
95Co5Mn/CNT	86.6	11.8	6.7	81.5	70.6	6.5	0.74	0.751
90Co10Mn/CNT	79.8	13.3	8.4	78	62.2	5.9	0.72	0.734
85Co15Mn/CNT	73.2	14.1	9.4	76.5	56.0	5.2	0.69	0.715
80Co20Mn/CNT	66.3	15.0	10.5	74.5	49.4	4.5	0.66	0.692
Mn/CNT	31.5	17.0	11.1	11.6	36.5	8.9	0.40	0.372

The monometallic cobalt catalyst resulted in low selectivity to methane and light gaseous hydrocarbons while high selectivity of C₅₊ hydrocarbons. On the other hand, for lighter hydrocarbons, the monometallic Mn/CNT catalyst showed very high selectivity. Table 5 shows that manganese incorporation in the cobalt catalyst changed the distribution of the product. Adding 5 wt% and 10 wt% of Mn to the cobalt catalyst increased selectivity of CH₄ and C₅₊. The addition of 15% and 20% of manganese to cobalt catalysts resulted in an increase in CH₄ selectivity from 11.8% to 15.0% and a decrease in C₅₊ hydrocarbon selectivity from 81.5% to 74.5%. The hydrocarbon synthesis mechanism of the Co and Mn catalyst includes three steps, namely initiation, propagation, and termination responses. Consequently, the greater average molecular weight of products acquired using a monometallic cobalt catalyst was due to the development of the secondary chain of re-adsorbed α -olefins, whereas the development of the secondary chain was negligible for manganese catalysts over propagation steps [53]. Mn enriched on the surface of bimetallic catalysts and the catalyst took on the properties of the metal in bimetallic catalysts with higher loads of manganese, thus reducing the growth of the chain by reabsorbing α -olefins and secondary reactions. It was also suggested that the formation of Co–Mn alloys in bimetallic catalysts reduces non-alloyed cobalt and subsequently reduces chain development by re-adsorption of α -olefins and secondary reactions [41]. As demonstrated in Table 5, Mn/CNT monometallic catalyst olefin selectivity is 3.5 times greater than the selectivity of Co/CNT monometallic

catalyst. Mobility in the presence of manganese hydrogen is suggested to be restricted by blocking low edge and corner sites for dissociative hydrogen adsorption [54].

Variations of CO conversion with time on stream (TOS) for Co/CNT, 95Co5Mn/CNT, 90Co10Mn/CNT, 85Co15Mn/CNT, and 80Co20Mn/CNT catalysts were studied. Catalysts have different stability within a time period of 48 h. The 95Co5Mn/CNT catalyst sample is more stable compared to that of other formulations of catalyst samples, showing a 2% decrease in conversion during 48 h of reaction. The stability of the catalyst may be attributed to the Mn percentage, the extent of functional groups, and defects, structure, and morphology of CNT supports [24,55].

4. Conclusions

The effects of the Co/Mn proportion on bimetallic catalyst activity and selectivity of Co–Mn were explored using CNT with distinctive characteristics such as high surface area and uniform pore structure with minor metal–support interaction. A series of carbon nanotube catalysts containing Mn and Co were prepared and FTS studies showed that the two metals had different catalytic properties when intimately mixed together compared to monometallic catalysts containing only one of the Mn and Co metals. The strong electrostatic adsorption (SEA) method resulted in a well-dispersed, low-co-charge CNT support Co nanoparticle. The low amounts of Mn enhanced the reducibility and dispersion of the Co–Mn bimetallic catalysts. The FTS reaction rate and percentage CO conversion were enhanced with the addition of manganese to the cobalt catalyst and the highest CO conversion rate for the 95Co5Mn/CNT catalyst was 86.6%. The WGS reaction rate was increased by adding manganese to the cobalt catalyst. However, the WGS reaction rate at low Mn values was not significantly increased. The monometallic cobalt catalyst showed relatively high selectivity (59.1%) towards C₅₊ hydrocarbons. Adding a small amount of manganese changed the product's selectivity. The monometallic manganese catalyst showed C₅₊ hydrocarbons with the lowest selectivity of 11.6%. The olefin to paraffin ratio in FTS products increased 2% with the addition of manganese and decreased when manganese increased from 5% to 20%. The monometallic manganese catalyst showed a minimum olefin to paraffin ratio of 0.40.

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