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Waste plastics recycling for producing high-value carbon nanotubes: Investigation of the influence of Manganese content in Fe-based catalysts

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Abstract

Thermo-chemical conversion is a promising technology for the recycle of waste plastics, as it can produce high-value products such as carbon nanotubes (CNTs) and hydrogen. However, the low yield of CNTs is one of the challenges. In this work, the addition of Mn (0 wt.%, 1 wt.%, 5 wt.%, and 10 wt.%) to Fe-based catalyst to improve the production of CNTs has been investigated. Results show that the increase of Mn content from 0 wt.% to 10 wt.% significantly promotes CNTs yield formed on the catalyst from 23.4 wt.% to 32.9 wt.%. The results show that Fe-particles in the fresh catalysts are between 10-25 nm. And the addition of Mn in the Fe-based catalyst enhanced the metal-support interactions and the dispersion of metal particles, thus leading to the improved catalytic performance in relation to filamentous carbon growth. In addition, the graphitization of CNTs is promoted with the increase of Mn content. Overall, in terms of the quantity and quality of the produced CNTs, 5 wt.% of Mn in Fe-based catalyst shows the best catalytic performance, due to the further increase of Mn content from 5 wt.% to 10 wt.% led to a dramatic decrease of purity by 10 wt.%.

Keywords: Waste plastics; carbon nanotubes; Mn-catalyst; thermo-chemical processing; pyrolysis

1. Introduction

Nowdays, plastics are used in various aspects, from household goods such as packaging, clothing, electrical devices, to industrial applications such as automotive parts and insulations (Lettieri and Al-Salem, 2011). The vast demand for plastic results in increasing plastic production year by year. In 2016, plastic production reached 330 million tons and will double within the next 20 years under the current estimationed growth rate (Lebreton and Andrady, 2019). The extensive use of plastics generates a large amount of wastes. These waste plastics cause severe environmental pollution if they were not well managed. The general methods for plastics waste management include landfill, energy recovery and recycling. Landfill is the most common method for plastic waste treatment in developing countries due to the cheap cost. Even in Europe, ~31 % of waste plastics still goes to land fill, wasting energy stored in the plastic and also causing severe environmental challenges (Drzyzga and Prieto, 2019; Lebreton and Andrady, 2019). In principle, recycling of plastic waste provides a more economical and environmental-friendly solution. However, current state of the art technologies of plastic wastes recycling mostly produce low-value products, such as cricks and road construction materials. Therefore, converting waste plastics into high-value products such as carbon nanotubes (CNTs) is a promising alternative for plastic waste management.

Since its discovery by Iijima in 1991 (Iijima, 1991), the extraordinary mechanical and electrical properties of CNTs have allowed it to find a variety of potential applications, such as drug delivery (Bianco et al., 2005), energy storage (Landi et al., 2009), materials strengthening (Andrews et al., 2002), etc. As a result, CNTs production from catalytic pyrolysis of plastic waste has been obtaining increasing interest. The key component to plastic pyrolysis is the catalyst which determines both the yield and quality of the produced CNTs.

In the chemical vapour deposition (CVD) synthesis of CNTs from various carbon feedstocks, Fe, Co and Ni are the most effective and widely used catalysts (Shah and Tali, 2016). The using of different catalysts could lead to the different properties and yield of CNTs. Lee et al. investigated the influence of Fe, Co and Ni-silica supported catalysts and reported that Fe catalyst resulted in the best crystallinity of produced CNTs. Sivakumar et al. reported that the produced CNTs over Ni catalyst have higher thermal stability than Fe catalyst (Sivakumar et al., 2011). In addition, the morphology and quality of the produced CNTs were also strongly affected by carbon feedstocks (Yan et al., 2015). In the catalytic synthesis of CNTs using plastic as carbon source, extensive researches have also been conducted on a range of metals e.g. Fe (Wu et al., 2017a), Ni (Yao et al., 2018) and Co (Acomb et al., 2016). Acomb et al. produced CNTs using Fe/Al₂O₃ catalyst from catalytic pyrolysis of LDPE (Low-Density Polyethylene) and obtained carbon deposition yielded 26 wt.% (Acomb et al., 2016). Yao et al. reported using Fe/ α -Al₂O₃ and Fe/ γ -Al₂O₃ catalyst to produce CNTs from real world plastics, and the carbon yielded 35.2 and 32.6 wt.%, respectively (Yao et al., 2018). In Wu et al's work, Fe/SiO₂ catalysts were used to produce CNTs with carbon yield 29 wt.% from PP (Wu et al., 2017a). In the previous work, compared to Ni or Co based catalyst, Fe-based catalysts lead to a higher yield of carbon from catalytic conversion of plastics, which is owing to the higher carbon solubility and higher carbon diffusion rate of iron nanoparticles (Deck and Vecchio, 2006) as well as the appropriate strength of metal-support interactions (Acomb et al., 2016).

Mn acting as an effective promoter was used in a variety catalytic reactions, such as the

Fischer–Tropsch process (Bezemer et al., 2006; Ding et al., 2013; Xu et al., 2013a; Zhao et al., 2012), volatile organic compounds oxidation (Tang et al., 2014), and the decomposition of nitrous oxides (Jia et al., 2016; Karásková et al., 2010). As for the synthesis of CNTs, Mn as a promoter in Ni-based and Co-based catalysts have also been reported from various carbon feedstocks (Zein and Mohamed, 2004)(Nahil et al., 2015)(Wu et al., 2017b). The promoting effects of Mn in Ni-based catalyst for CNTs synthesis from methane were reported by several researchers. For example, Zein et. al reported Mn-Ni/TiO₂ catalysts prepared by three different methods for the production of hydrogen and CNTs from methane (Zein and Mohamed, 2004). However, only a fixed content of Mn (15 wt.%) was used in the research, and the reasons for the catalytic performance was not clear. Ran et. al further investigated the doping effect of Mn on CNTs formation in the presence of Ni/MgO catalysts with varied Mn content. It was found that the addition of Mn to the Ni/MgO catalyst significantly increased the carbon yield, with the highest carbon yield produced by the catalyst with Mn:Ni a molar ratio of 0.2:1 (Ran et al., 2014). In addition, Becker et al. reported that Mn-Co catalysts with Mn:Co molar ratio of 1:1 led to the highest CNTs yield using ethene as carbon source (Becker et al., 2011). He et. al applied Mn-Fe/MgO catalyst to improve the chirality distribution of the produced single-walled CNTs using CO as carbon source (He et al., 2016).

Mn's promoting effects have also been investigated in the CNTs synthesis from waste plastics. In Nahil et. al's work, a variety of metals (Zn, Mg, Ca, Ce, Mo, Mn, etc.) added into Ni-based catalysts have been investigated for the catalytic conversion of waste plastics (polypropylene) into CNTs (Nahil et al., 2015). It was found that the addition of Mn into Ni-based catalyst resulted in the highest yield of CNTs. Further work by Wu et al. investigated the effects of Mn content on CNTs synthesis in the Ni-based catalyst. The Mn-Ni/Al₂O₃ catalyst with Mn:Ni a molar ratio of 2:2 produced a higher yield of carbon compared to Mn:Ni with a molar ratio of 2:1 in the synthesis of CNTs using waste plastics (polypropylene) as carbon feedstock.

Owing to the great catalytic performance of Fe-based catalyst and Mn as a promising promoter in CNTs formation from plastics, there is a potential of further increasing CNTs production and quality by doping Mn into Fe-based catalyst during catalytic conversion of waste plastics. Therefore, in this work, we report the influence of Mn content in the Fe-based catalyst for CNTs production from catalytic pyrolysis of waste plastics. This work aims to optimise the development of Fe-based catalysts by adding Mn in relation to CNTs production from waste plastics.

2. Experimental

2.1 Materials and preparation of catalyst

The plastic raw material used in this study was recycled polypropylene (PP) pellet obtained from regain polymer Ltd. with a diameter of ~2mm. The chemicals Mn(NO₃)₂•H₂O (98%, Sigma-Aldrich, cat. no. 288640) and Fe(NO₃)₃•9H₂O (≥98%, ACS reagent, Sigma-Aldrich, cat. no. 16828) were used as starting materials. Al₂O₃ (≥98%, puriss, Sigma-Aldrich, cat. no. 11028) with particle size around 10 μm is used as the catalyst support. All materials were used directly without any pre-treatment. MnFe/Al₂O₃ catalysts were prepared by a wet impregnation method. The catalysts

contain 10 wt.% of Fe. The content of Mn is 0 wt.%, 1 wt.%, 5 wt.% and 10 wt.%, respectively. And the corresponding catalyst is assigned as 0Mn10Fe, 1Mn10Fe, 5Mn10Fe and 10Mn10Fe, respectively. For comparison, a catalyst with 10 wt.% Mn without Fe (10Mn0Fe) was prepared use the same method.

During catalyst preparation, the required amount of $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 100 ml of deionized water, and the mixture solution was stirred for ~ 0.5 h until the chemicals were fully dissolved. The required amount of Al_2O_3 was then slowly added into the mixture solution and stirred for ~ 1 h. After that, water was removed by evaporation at 90°C , followed by drying in an oven at 105°C overnight to remove the remaining water. Finally, the dried catalyst precursors were grounded into a fine powder and then were heated in the air atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ to 500°C for 3 h of calcination.

2.2 Catalytic pyrolysis of plastic waste into CNTs

The catalytic pyrolysis of plastic waste into CNTs was performed in a two-stage reactor in this study. Fig. 1 shows the schematic diagram of this reaction system. The first-stage reactor consists of a horizontal quartz tube placed in a tubular furnace for PP pyrolysis. The generated vapor was carried by N_2 with a flow rate of 100 ml min^{-1} and after condensation, the non-condensed products passed through the second-stage of the reactor.

For each run of the experiment, 2 g of PP was located inside an aluminium boat in the centre of the first-stage reactor, and 0.5 g of catalyst supported by ~ 30 mg of quartz wool was located in the centre of the second-stage reactor. The reaction system was purged by N_2 for ~ 10 min before the second-stage reactor started to heat from room temperature to 800°C with a heating rate of $40^\circ\text{C min}^{-1}$. When the second-stage reactor reached the set point temperature, the first-stage reactor containing 2 g of PP started to heat from room temperature to 200°C with a heating rate of $40^\circ\text{C min}^{-1}$, followed by heating from 200°C to 500°C with a heating rate of $10^\circ\text{C min}^{-1}$. After ~ 1 h of reaction time, the reaction system was slowly cooled down to room temperature under N_2 protection, and the reacted catalyst together with the produced CNTs were collected for further characterisations. The Fe-based catalysts with different Mn contents associated with the production of CNTs were studied.

Fig. 1. Schematic diagram of the two-stage reaction system.

2.3 Characterisation of fresh and reacted catalyst

TA Instruments TGA 2950 thermogravimetric analyser (TGA) was used to analyse the temperature programme reduction (TPR) of the fresh catalyst to observe the reduction of the catalyst metal. Under a mixed gas of H₂ and N₂ gas (5 vol.% : 95 vol.%), ~50 mg of catalyst was heated from room temperature to 100 °C at a heating rate of 10 °C min⁻¹ and held for 10 min, then the temperature increased to 950 °C under at the same heating rate to record the TPR curve.

Temperature programme oxidation (TPO) analysis for the reacted catalysts was conducted by the same TGA 2950 equipment using air gas to measure the amount of carbon formed on the reacted catalyst and to distinguish different types of carbons, such as amorphous carbons or graphite. For each TPO process, ~30 mg of reacted catalyst sample was heated to 800 °C in air at a heating rate of 15 °C min⁻¹. The fresh and reacted catalysts were also characterized by a Panalytical X-ray diffraction (XRD) equipment with a scanning step of 0.033° using Cu•K α 1 radiation in the range from 5° to 80° and the data was analysed with Highscore software. The strongest peak was chosen to calculate the crystallite size by Scherrer equation. The surface morphology and diameter of the metal particles of the catalysts were observed with a FEI Quanta FEG Oxford Ex-ACT scanning electron microscope (SEM) and a Jeol 2100 LaB6 transmission electron microscope (TEM). The WITec Alpha 300R Confocal Raman Microscope equipped with a 532 nm diode laser with an output power of 30 mW was used to perform Raman spectroscopic analysis of the reacted catalyst.

3. Results and discussion

3.1 Characterization of fresh catalysts

XRD results of the prepared Fe-based catalysts with varied Mn contents are shown in Fig. 2. In general, the diffraction patterns of all four catalysts are dominated by the characteristic peaks of α -Fe₂O₃ at 4.2°, 33.3°, 35.7°, 41.05°, 49.71°, 54.36°, 62.74°, 64.30° 2 θ , indicating that the main composition of the catalysts are α -Fe₂O₃. For the 0Mn10Fe catalyst, the diffraction patterns only consist of peaks corresponding to α -Fe₂O₃ and Al₂O₃. For the Mn-doped catalysts, the XRD data show weak diffraction of manganese oxides, which is in good agreement with literatures (Feyzi and Jafari, 2012; Lee et al., 1991; Nasser et al., 2018; Yang et al., 2005). This might be due to Mn was present as amorphous or highly dispersed on the surface of the Al₂O₃ support (Nasser et al., 2018).

The size of the α -Fe₂O₃ crystallite phase was calculated using the Scherrer equation. For the 0Mn10Fe catalyst, the crystallite size is 107.1 nm. Interestingly, it is found that the crystallite size of 1Mn10Fe, 5Mn10Fe and 10Mn10Fe catalyst are much smaller, at 14.0 nm, 8.4 nm, and 30.3 nm, respectively. It is indicated that an appropriate amount of Mn dopant could significantly improve the dispersion of iron in the catalyst. The crystallite size of the 10Mn10Fe catalyst is larger than the 5Mn10Fe catalyst, which could be resulted from the excessive amount of Mn dopant in the catalyst. It is now well-established that the size of the catalyst particles are crucial for CNTs formation and that larger particles often exhibit lower catalytic activities due to the reduced active-surface area (Acomb et al., 2016; Liu et al., 2009). Therefore, the above findings demonstrate that an appropriate amount of Mn is required to be added to the Fe-based catalyst in terms of the catalytic conversion of waste plastics to form CNTs.

Fig. 2. X-ray diffraction of the fresh Fe-based catalysts with different amount of (Mn 0Mn10Fe, 1Mn10Fe, 5Mn10Fe and 10Mn10Fe).

The H₂-TPR results for the four catalysts are shown in Fig. 3. Several reduction peaks are obtained since both Fe and Mn elements possess several types of oxide forms and the reduction of Fe₂O₃ and Mn₂O₃ proceed subsequently. Hydrogen reduction of Fe₂O₃ involves two or three steps according to different reduction temperatures (Pineau et al., 2006): when the reduction temperature is below 570 °C, wüstite FeO was formed as an intermediate product before the formation of Fe, as illustrated in Eq. (1); when the reduction temperature is above 570 °C, Fe₂O₃ reduced into Fe₃O₄ and then directly reduced into Fe, as shown in Eq. (2):

As indicated in Fig. 3, the 0Mn10Fe catalyst undergoes two stages of reduction. ~0.68 wt.% weight loss occurred in the first stage and ~5.5 wt.% weight loss occurred in the second stage. The first reduction peak at 420 °C can be attributed to the reduction of α -Fe₂O₃ to Fe₃O₄. The second broad peak as illustrated in the range of 450-750 °C can be attributed to the subsequently reduction of Fe₃O₄ to FeO and Fe following Eq.(1) process. 1Mn10Fe have three reduction stages, which have a weight loss of 0.47 wt.%, 0.69 wt.% and 2.47 wt.%, respectively. 1Mn10Fe shows a major reduction peak in the first stage for the reduction of α -Fe₂O₃ to Fe₃O₄ which shifted towards higher temperature compared to 0Mn10Fe. Meanwhile, the first stage weight loss for 1Mn10Fe is lower than that compared to 0Mn10Fe. These suggesting that the Mn-doped catalyst is more resistant to the reduction and the metal-support interactions is enhanced with the addition of Mn. The new peak appearing at 540 °C for 1Mn10Fe catalyst indicates that the reduction of Fe₃O₄ to Fe via FeO is further stabilized by MnO (Leith and Howden, 1988; Yang et al., 2005, 2004). The weight loss of four reduction stages for the 5Mn10Fe catalyst are 0.58 wt.%, 0.61 wt.%, 0.92 wt.% and 2.4 wt.%, respectively. And the 10Mn10Fe catalyst shows an obvious increase of weight loss in the first two reduction peaks, which are 1.4 wt.% and 1.3 wt.%, respectively. For the third and fourth reduction stages,

it shows a similar weight loss value compared to the 1Mn10Fe and 5Mn10Fe catalysts. The new reduction peak appears at ~ 370 °C for the 5Mn10Fe and 10Mn10Fe catalysts can be attributed to the large amount of Mn_3O_4 which is reduced into Mn with MnO as intermediates. This indicates the overall weight loss is increased from 3.63 wt.% to 6.1 wt.% when the Mn content increases from 1 wt.% to 10 wt.% in the catalyst, but the corresponding reduction weight loss for Fe_3O_4 is similar. In addition, the major $\alpha\text{-Fe}_2\text{O}_3$ reduction peak for the 5Mn10Fe and 10Mn10Fe catalysts shifts towards higher temperature at ~ 430 °C compared to the 1Mn10Fe catalyst, suggesting that increasing the Mn loading from 0-5 wt.% improves the metal-support interactions but the further increase of Mn loading to 10 wt.% has slight impacts on the metal-support interaction.

Fig. 3. TPR (a) and DTG-TPR (b) profiles of the fresh Fe-based catalysts with varied amount of Mn in the catalysts (0Mn10Fe, 1MnFe, 5Mn10Fe and 10Mn10Fe).

3.2 The production of CNTs

3.2.1 Temperature programmed oxidation (TPO) of the reacted catalysts

TPO results of the reacted catalysts (0Mn10Fe, 1MnFe, 5Mn10Fe and 10Mn10Fe) are shown in Fig.4. Based on previous work, the weight loss of amorphous carbons and filamentous carbons can be distinguished using oxidation temperature due to their different oxidation properties: the weight loss occurred before 600 °C corresponds to the oxidation of amorphous carbon, while the weight loss occurred after 600 °C is related to the oxidation of filamentous carbon (assumed as CNTs in this study) (Wu and Williams, 2009; Yang et al., 2015; Zhang et al., 2017). From Fig. 4(a), a slight increase of the catalyst weight between 350 and 500 °C is observed due to the oxidation of Mn and Fe. For the reacted 10Mn0Fe catalyst, no weight loss is observed, which indicates that almost no carbons are deposited on the surface of the reacted catalyst. Therefore, it is demonstrated that the 10Mn0Fe catalyst without Fe is inactive for carbon formation. However, the remaining four Fe-based catalysts show a significantly increase of weight loss with increasing Mn content and the 10Mn10Fe catalyst gives the highest carbon formation (~ 41.5 wt.% of the total catalyst), as shown in Fig.4(a). It is indicated that Fe is the active sites and Mn promotes the catalytic conversion of waste PP to form carbon. Other

researchers have obtained similar results, that is, Mn acted as a promoter for the production of CNTs in Ni-based (Ran et al., 2014; Zein and Mohamed, 2004) and Co-based catalysts (Becker et al., 2011).

The yield of amorphous and filamentous carbons are determined by the TGA-TPO curves according to their different oxidation temperatures/thermal stabilities. The carbon yield of amorphous and filamentous carbons for each catalyst is obtained according to Eq.(3). This is calculated based on the weight loss of each reacted catalysts on TGA-TPO results as shown in Fig. 4. And the calculation results are shown in Fig. 5(a).

$$m_i = \frac{w_i}{M} \times 100\% \quad (3)$$

Where ‘ i ’ means amorphous or filamentous carbons. The ‘ w_i ’ represents the weight of amorphous or filamentous carbons deposited on the surface of reacted, ‘ M ’ represents the mass of reacted catalyst, and ‘ m_i ’ means the yield of amorphous or filamentous carbons, respectively.

Fig. 4. TGA-TPO (a) and DTG-TPO (b) patterns of reacted catalyst with different amount of

Mn addition in the catalysts (0Mn10Fe, 1MnFe, 5Mn10Fe, 10Mn10Fe and 10Mn0Fe).

As shown in Fig. 5(a), the addition of 1 wt.% of Mn into Fe-based catalyst shows slight increase on carbon content. A further increase of Mn to 5 wt.% and 10 wt.% results in a significantly increase of both amorphous and filamentous carbons. It is worth noting that when the Mn content is increased from 1 wt.% to 5 wt.%, the yield of filamentous carbons significantly increases by ~6 wt.%. However, as shown in Fig. 5, when the Mn content is further increased from 5 wt.% to 10 wt.%, the yield of filamentous carbon is only increased by ~2.5 wt.% while amorphous carbon increases by ~5 wt.%.

The mass ratio between amorphous and filamentous carbons for different catalysts is calculated according to Eq.(4) based on the carbon yield calculated from Eq.(3), and the calculation results are shown in Fig. 5(b).

$$M_i(\%) = \frac{m_i}{\sum m_i} \times 100\% \quad (4)$$

Where the ‘ M_i ’ mean the mass ratio of filamentous and amorphous carbon.

As shown in Fig. 5(b), the mass ratios of amorphous and filamentous carbons generated on the 0Mn10Fe, 1Mn10Fe and 5Mn10Fe catalysts are similar. However, when the Mn content

reaches 10 wt.%, the mass ratio of unwanted amorphous carbons is significantly increased to 20.9 wt.%. Although increasing the addition of Mn from 0-10 wt.% promotes carbon formation for both filamentous and amorphous carbons as shown in Fig. 5(a), to some extent, the influence of Mn addition on the mass ratio of filamentous and amorphous carbons is different. The addition of Mn in the range of 0-5 wt.% shows less influence on the mass ratio of produced filamentous carbons while a further addition of Mn to 10 wt.% dramatically reduces the mass ratio of filamentous carbons. It is suggested that the addition of Mn in the range of 0-5 wt.% promotes CNTs growth and the further increase of Mn content favours the formation of amorphous carbons. In addition, the DTG-TPO results in Fig.4(b) show that the oxidation peak for the 10Mn10Fe catalyst occurs at lower temperature compared to 0Mn10Fe, 1Mn10Fe and 5Mn10Fe. It is indicated that a lower oxidation peak is corresponding to a higher mass ratio of amorphous carbons.

Fig. 5. (a) Amorphous/filamentous carbon yield on each of the reacted catalysts. (b) Mass ratio of amorphous and filamentous carbons on each catalyst.

3.2.2 X-ray diffraction (XRD) of reacted catalysts

Fig. 6 shows the XRD patterns of the four reacted catalysts. The Fe crystallite size is obtained from Scherrer equation. The results show that the Fe crystallite size of the four reacted catalysts is quite similar, which are 14.5 nm, 19.9 nm, 19.9 nm, and 19.9 nm for the 0Mn10Fe, 1Mn10Fe, 5Mn10Fe and 10Mn10Fe catalyst, respectively. From Fig. 6, it can be seen that the four reacted catalysts mainly contain iron carbides (Fe_3C and Fe_5C_2) and Fe phases after reaction, suggesting that $\alpha\text{-Fe}_2\text{O}_3$ was fully reduced to Fe by the generated gas and then the reduced Fe was partially carbonised. Similar phase transformation of $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3C was also reported in the recent study (Zhang et al., 2020). For the 5Mn10Fe and 10Mn10Fe catalysts, there are additional peaks detected in the XRD patterns, indicating the existence of MnO phase. In addition, the peak intensity of Fe_3C phase is decreased while the Fe_5C_2 intensity is increased with the increase of Mn content in the Fe-based catalyst. It is suggested that Mn in the catalyst promote the carburization of Fe_5C_2 rather than Fe_3C , hence, the carbon solubility per iron atom is reduced. Similar effects on hindering the carburization of Fe have also been reported (Lee et

al., 1991; Nasser et al., 2018; Xu et al., 2013b). The lower carbon content accelerated intermediate carbides to reach the carbon concentration required for graphite precipitation, hence to promote CNTs growth (Deck and Vecchio, 2006).

Fig. 6. X-ray diffraction of the reacted Fe-based catalysts contain Mn.

3.2.3 SEM and TEM results of the catalysts

Fig. 7 shows the SEM results of the four fresh and reacted catalysts. It is indicated that the overall particle of the fresh catalyst is around 10 μm . After catalytic conversion of waste plastics, an abundance of filamentous carbons could be clearly observed on the catalysts surface. The morphologies of the formed filamentous carbons on the four reacted catalysts were further investigated by TEM as shown in Fig. 8. The results illustrate the filamentous carbons with different structures in terms of size and homogeneity are formed over the four catalysts. Obviously, the metal particles are wrapped inside the tip of the CNTs, which is consistent with the tip growth mechanism of CNTs (Amelinckx et al., 1994). The formed CNTs with comparatively unsmooth and unhomogeneous structures are clearly observed for the 5Mn10Fe and 10Mn10Fe catalysts. The CNTs produced by the four catalysts have similar inner diameters (between 10-25 nm), which is consistent with the crystallite size of the active metal particles (15-20 nm) within the catalysts calculated from XRD results. It is demonstrated that the size of the CNTs is directly correlated to the particle size of active sites (Kotov et al., 2019)(Cheung et al., 2002; Ding et al., 2004; Nerushev et al., 2003). Interestingly, adding Mn to Fe-based catalysts seems to improve the radical growth of CNTs. As shown in Fig.8, the outer diameters of CNTs produced by the 0Mn10Fe and 1Mn10Fe catalysts are similar, ranging from 15-60 nm, while the outer diameter of CNTs formed on 5Mn10Fe and 10Mn10Fe catalysts are larger (30-115 nm). This may be attributed to the Mn contents affected the supersaturation degree of carbon atoms in the Fe nanoparticle as described in a recent study (Hayashi and Kohno, 2020).

327

328

329

(a)0Mn10Fe

330

(b)1Mn10Fe

331

332

(c) 5Mn10Fe

(d) 10Mn10Fe

Fig. 7. SEM morphology analysis of the fresh (left) and reacted (right) Mn containing Fe-based catalysts: (a) 0Mn10Fe (b) 1Mn10Fe, (c) 5Mn10Fe and (d) 10Mn10Fe.

(a) 0Mn10Fe

(b) 1Mn10Fe

(c) 5Mn10Fe (d) 10Mn10Fe

Fig. 8. TEM of the carbon deposition on the reacted Mn containing Fe-based catalysts: (a) 0Mn10Fe (b) 1Mn10Fe, (c) 5Mn10Fe and (d) 10Mn10Fe.

3.2.4 Raman spectra of the reacted catalysts

Raman spectroscopy analysis was performed to characterise the structure of amorphous and/or graphitic carbon and estimate the purity of CNTs (DiLeo et al., 2007; Ferrari and Robertson, 2004). As shown in Fig.9, the Raman spectrum at wavelength of 1000-3000 cm^{-1} are presented to compare the carbons produced from the four Fe-based catalysts with varied Mn contents from 0-10wt.%. The Raman spectra are dominated by three vibration bands characteristic of the Raman vibrations of carbonaceous materials: the D band at $\sim 1345 \text{ cm}^{-1}$ arises from amorphous carbon or disordered carbon within structural defects; the G band at $\sim 1573 \text{ cm}^{-1}$ arises from the sp^2 stretching vibration of the graphitic structures and is characteristic of graphitic samples; and the G' band at $\sim 2680 \text{ cm}^{-1}$ arises from the second-order scattering process of two phonons, indicating the purity of carbons (Dresselhaus et al., 2005; Saito et al., 2003). The I_D/I_G ratio obtained by the normalizing the intensity of the D band to the G band could be used to evaluate the graphitization of carbons. As shown in Fig. 8, as the Mn content increases from 0 wt.% to 10 wt.%, the carbon I_D/I_G ratio decreases from 0.60 to 0.40, suggesting that a higher amount of Mn doping could lead to a higher ratio of graphitic carbons. The $I_{G'}/I_G$ ratio could be used to estimate the purity of CNTs (DiLeo et al., 2007). The $I_{G'}/I_G$ ratios for 0Mn10Fe, 1Mn10Fe and 5Mn10Fe are in a similar range, which indicates that the purity of the CNTs produced by the three catalysts is similar. The smallest $I_{G'}/I_G$ ratios for the 10Mn10Fe catalyst at 0.46 correspondes to the lowest purity of CNTs, which is agreement with the TPO results shown in Fig. 5(b). Therefore, when the addition of Mn in the catalyst is below 10 wt.%, the graphitization of the produced carbon could be improved. However when excessive Mn (10 wt.%) is added into the iron-based catalyst, the purity of the produced carbon could be reduced.

Table 1 shows the comparison of our work with other different Fe-based catalyst in literatures. The detailed carbon yield, as well as the morphology and quality of produced CNTs are presented. It is indicated that 10Mn10Fe produces a high yield of carbons in comparing with other works. In addition, a large portion of the generated gases were trapped in condensation system before passing through the second stage of reactor, which decreases the carbon feedstock for CNTs growth, thus, could decrease the 10Mn10Fe catalyst capacity to produce the highest carbon yield. The excellent catalytic performance could be partially attributed to the addition of Mn. In addition, the CNTs grow on 10Mn10Fe catalyst have the lowest I_D/I_G ratio value, indicating that the produced CNTs are better graphitized than other catalysts. This could be also partially attributed to the promoting graphitization of Mn in the Fe-based catalysts.

Fig. 9. Raman spectra of reacted catalysts.

Table 1

Comparison of carbon yield and Raman results between our research results and reports in literatures.

Feedstock	Catalyst	Carbon yield (wt.%) ^a	I _D /I _G	Ref.
PP	10Mn10Fe	41.5	0.4	This work
LDPE	Fe/Al ₂ O ₃	34.2	0.51	(Acomb et al., 2016)
Waste tires	Fe/Al ₂ O ₃	21.9	0.89	(Zhang et al., 2015)
PP	Fe/Cordierite	3	-	(Wang et al., 2019)
Realworld plastics	Fe/□-Al ₂ O ₃	41.3	0.64	(Yao et al., 2018b)
	Fe/□-Al ₂ O ₃	39.5	0.62	
PP	Fe/SiO ₂ -S	39.4	-	(Wu et al., 2017a)
	Fe/SiO ₂ -L	42.0	-	

^a Obtained from the recalculation of carbon yield reported from temperature programme oxidation analysis.

Conclusion

In this study, the addition of Mn into Fe-based catalysts with content at 0 wt.%, 1wt.%, 5 wt.% and 10 wt.% have been investigated for catalytic pyrolysis of PP into CNTs. Mn is an effective promoter in the Fe-based catalyst for CNTs growth from catalytic pyrolysis of PP. The enhanced metal-support interactions by Mn addition leads to a higher yield of carbons. The dispersion of iron nanoparticles is also enhanced by Mn, inhibiting the sintering of iron particles.

In addition, the iron oxide phase is stabilized by Mn addition, therefore contributing to the stability of catalytic Fe sites. Meanwhile, the catalyst with higher Mn content favours the formation of carbides at lower carbon concentration which promotes graphite precipitation from carbides intermediates. Owing to these effects, the yield and graphitization degree of the produced CNTs increases as Mn loading increases. However, the increased Mn loading in Fe-based catalyst has negative influence on the purity of produced CNTs. Although the 10Mn10Fe catalyst produces the highest carbon yield (41.58 wt.%) than other catalysts, the mass ratio of CNTs is much lower than the 5Mn10Fe catalyst.

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