

22 loading produced more hydrogen and deposited carbon, due to higher cracking ability
23 and the relatively lower interaction between active sites and support. The presence of
24 Ni in Ni-Fe bimetallic catalyst enhanced the thermal stability and graphitization
25 degree of produced carbons. The thermal quality of filamentous carbons might be
26 associated with carbon defects.

27 **Keywords:** waste plastics, hydrogen, carbon nanotubes, Ni-Fe bimetallic catalyst

28

29 **1. Introduction**

30 The global demand for plastic increases annually as the rapid economic
31 development and higher standard of living. However, the increased use of plastic
32 materials produces substantial quantities of plastic and brings serious environmental
33 problems. In China, approximately 18 million tons of plastic wastes were generated in
34 2015 [1]. It was reported that 25 million tonnes of wastes plastics are generated
35 annually in Europe, and more than 30% of post-consumer waste plastics end up in
36 landfill or incineration [2, 3].

37 Energy recovery like pyrolysis of plastics for chemical products is a promising
38 way to exploit the full potential of waste plastics. The thermal and catalytic pyrolysis
39 of plastics have been extensively studied in different reactors and under various
40 operational parameters, with the product distributions being dependent on these
41 conditions [4, 5]. Williams et al. [6] reported that pyrolysis waxes and oil enriched in
42 aliphatic composition could be produced from low density polyethylene using a
43 fluidised bed reactor. Ratnasari et al. [7] obtained a gasoline range hydrocarbons yield

44 of 83.15 wt.% from waste plastics in a staged catalysis system with MCM-41 and
45 ZSM-5. In addition, waste plastics could also be gasified [8] or co-gasified with
46 biomass [9] for hydrogen production at high catalyst temperatures. There has been
47 increasing interest in the pyrolysis-catalysis of waste plastics for high-value-added
48 products. Recently, carbon nanomaterials like CNTs have been obtained with
49 catalysis-pyrolysis of waste plastics [10, 11]. In that process, the valuable product
50 CNTs was produced instead of unwanted coke, which may lead to serious catalyst
51 deactivation. Furthermore, low-cost CNTs from waste plastics have been used as
52 reinforced material and resulted good performance of tensile and flexural strength,
53 presenting its great potential in industry application [12, 13].

54 CNTs, since it was firstly reported by Iijima in the early 1990s [14], has been
55 attracting considerable attentions because of the unique electrochemical and
56 mechanical properties [15]. It is known that CH_4 , C_2H_2 that from petrol industry, are
57 normally used as the carbon precursors for carbon nanotubes production using
58 chemical vapor deposition (CVD) method, which has been the dominant mode for
59 large production around the world [16-18]. As those small gases for CNTs production
60 can also be obtained from pyrolysis of waste plastics, it is an attractive way to apply
61 the pyrolysis-catalysis process to waste plastics for carbon nanotubes without overdue
62 consumption of non-renewable resources. Pyrolysis-catalysis process of waste plastics
63 for producing CNTs has similar principle as traditional CVD method using CH_4 ,
64 whereas, the main difference is that pyrolysis of plastic produces complicated carbon
65 sources. Ni based catalysts are reported to have good reactivity for C-C and C-H bond

66 cleavage, thus they are effective for polymers cracking and reforming reactions [19,
67 20]. Zhang et al. [21] found that Ni/Al₂O₃ showed higher activity to multi-walled
68 CNTs production along with higher H₂ yield compared to Co/Al₂O₃ and Cu/Al₂O₃ for
69 the catalytic reforming of waste tires. Yang et al. [22] synthesized CNTs with 20~30
70 diameter in a pilot-scale system using H-Ni/Al₂O₃ catalyst, demonstrating the
71 feasibility of Ni based catalyst for treating plastics continuously to generate high
72 value CNTs. Bulk carbon deposition of highly uniform carbon nanotubes as well as
73 55% of hydrogen yield were observed from methane catalytic decomposition with
74 Ni/La₂O₃ catalyst by Pudukudy et al. [23]. Besides, Fe based catalyst is also an
75 attractive catalyst with cheap and environmental friendly traits for the production of
76 carbon nanotubes. Acomb et al. [24] investigated the influence of different metal
77 catalysts for catalytic pyrolysis of LDPE, and found that Fe/Al₂O₃ gave the highest H₂
78 conversion (26.8 %) and carbon yield (26 wt.%), compared with Ni, Co and Cu based
79 catalysts. The moderate metal-support interaction and iron's large carbon solubility
80 contributed to its good performance.

81 For many catalysts studies, bimetallic catalysts by integrating different materials
82 are always suggested when considering both catalytic reactivity and energy
83 consumption. Some bimetallic catalysts like Ni-Mg, Ni-Mn [12] and Fe-Ru [25] have
84 been studied for the filamentous carbon production from pyrolysis-catalysis of
85 polymers. Ni was suggested to be responsible for the formation of carbon nanotubes
86 while Mn acted as a favorable promoter during carbon growth. The interaction
87 between Cu and Fe was found to enhance the nucleation of nanotubes over Fe as well

88 as minimize the bulk accumulation of carbon substrates [26]. The advantages of those
89 bimetallic or trimetallic catalysts always come from good stability, smaller metal
90 particle size and appropriate interaction or synergy between metals [27].

91 As for the Ni-Fe bimetallic catalysts, it has shown favorable performance for
92 some studies. Ni-Fe based on bio-char has been performed into biomass gasification
93 to increase tar conversion in an effective and economical way [28]. H₂ yield and
94 carbon conversion rate were increased when using Fe-Ni oxides were used for pine
95 sawdust gasification, resulting from the synergistic effect between Fe₂O₃ and NiO
96 [29]. Enhanced methane dehydrogenation and longer life-times activity of catalyst
97 were found by Shen et al. [30] when using Ni-Fe/Mg(Al)O for CNTs production from
98 methane. However, there are limited reports about using Ni-Fe bimetallic catalysts for
99 the coproduction of CNTs and H₂ from waste plastics. Furthermore, the role of Ni or
100 Fe on CNT and H₂ production are still unclear. Therefore, the catalytic pyrolysis of
101 waste plastic was investigated the bimetallic Ni-Fe catalyst for the simultaneous
102 production of H₂ and carbon nanotubes using a two-stage fixed bed reactor. In order to
103 understand the different catalytic reactivity, the prepared catalysts and solid products
104 were characterized by spectroscopic, temperature programmed and electronic
105 microscope analysis. Gas releasing behavior, H₂ yield, morphology and quality of
106 solid carbon at different Ni to Fe molar ratio were examined.

107

108 **2. Experimental material and methods**

109 2.1 Experimental materials

110 The waste plastics used in this research are some disposable drink cups, lunch
111 boxes, and plastic wraps (Mingjin Plastic Ltd, China), which are widely used for food
112 packing in daily life. They were crushed and mixed using a liquid nitrogen grinder
113 with particle size between 0.1 and 0.5 mm. The composition was 40 wt.% sample
114 bottles (mainly HDPE), 35 wt.% plastic bags (mainly LDPE), 20 wt.% preservative
115 boxes (mainly PP) and 5 wt.% lunch boxes (mainly PS). The ultimate analysis of the
116 material was 84.51 wt.% C, 13.85 wt.% H, 1.51 wt.% O and 0.13 wt.% S. Ash content
117 of the mixed plastics was less than 1 wt.%.

118 Bimetallic Ni-Fe catalysts with different Ni to Fe molar ratio were prepared
119 using impregnation method. Metal nitrates and gamma Al_2O_3 (obtained from Sigma
120 Aldrich, UK) were used as the materials. The initial metal loading was 10 wt.%. As an
121 example, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were firstly dissolved in ethanol with
122 Ni to Fe molar ratio of 1 to 3, then 10g gamma Al_2O_3 was added. Then the precursors
123 were stirred for 4 h using magnetic stirrer at 50 °C, and dried at 100 °C overnight,
124 followed by calcination at 800 °C for 3 hours holding time under air atmosphere with
125 a heating rate of 10 C min⁻¹. The other catalysts were prepared following the same
126 procedure, but with different Ni to Fe ratio. It need to be pointed out that no reduction
127 prior to the catalytic pyrolysis as the gases produced during pyrolysis-catalytic
128 process such as H_2 and CH_4 might reduce the metal oxides in situ [31]. The five
129 catalysts prepared here were denoted as NiFe13, NiFe12, NiFe11, NiFe21 and NiFe31
130 separately (corresponding to the molar ratio of Ni:Fe of 1:3, 1:2, 1:1, 2:1 and 3:1).

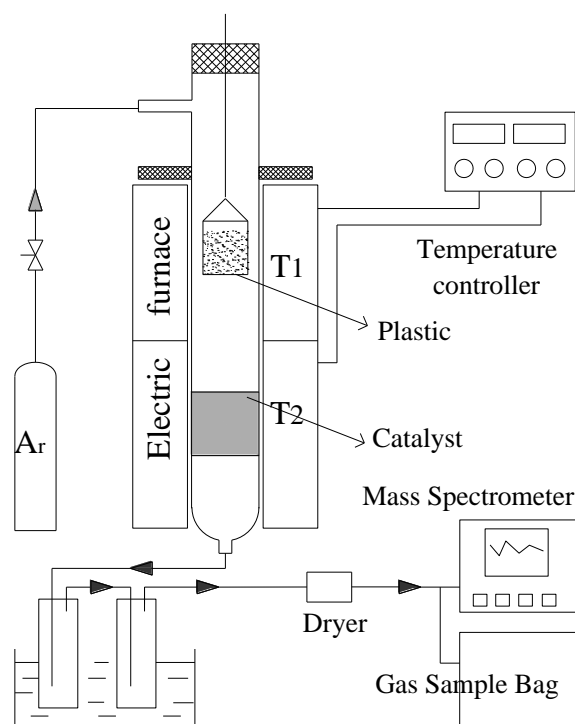
131

132 2.2 Experimental setup and procedure

133 The pyrolysis-catalytic process of waste plastics was carried out in a two-stage
134 fixed bed reactor (Fig. 1). The reaction system consists essentially of a quartz tube
135 reactor (I.D. 40mm) with two temperature ranges (upper: pyrolysis zone, 310 mm
136 height; under: catalysis zone, 310 mm height), a gas supplying system, gaseous
137 product condensing system with ice and water mixture, a gas cleaning system
138 followed by gas online and offline measurement system.

139 Before each experiment, 0.5g catalyst was supported by ~0.2g stainless steel
140 wire mesh on the top of a perforated plate, which was placed in the middle of second
141 stage, where the temperature was heated to 800 °C. A quartz basket with 1g waste
142 plastic was hold in the top of first reactor. High purity of Argon (99.99%) was
143 supplied as inert gas at 110ml min⁻¹. After the catalyst temperature reached to selected
144 temperature and kept stable, the basket containing plastic sample was introduced into
145 the middle of first stage, and the pyrolysis temperature was programmed to increase
146 from room temperature to 500 °C with a heating rate of 10 °C min⁻¹ and held at 500°C
147 for 15 min. After pyrolysis-catalytic process, condensable vapors were collected by a
148 two-stage ice-water condenser. A small branch of the non-condensable gases was
149 introduced into mass spectrometer (MS) (Ominstar TM—GSD320, Pfeiffer Vacuum,
150 Germany) to monitor gas evolution online with a data acquisition frequency of 1 s⁻¹.
151 The signals identified as the atomic mass units of 2, 16, 26, 28, 30, 44 corresponded
152 to the main produced gas H₂, CH₄, C₂H₂, CO+C₂H₄, C₂H₆ and CO₂ respectively,
153 according to the molecular weights of gases. The main stream was sampled with a 20

154 L gasbag, and gas composition was determined using a dual-channel gas
155 chromatograph (GC) (Micro-GC 3000A, Agilent Technology, USA) equipped with
156 thermal conductivity detectors. H₂, CO and CH₄ were detected by channel A
157 (molecular sieve 5A) and CO₂, C₂H₂, C₂H₄, C₂H₆ were measured by channel B
158 (polystyrene chromatographic column). Each experiment was repeated twice to ensure
159 the reliability of the results.



160

161 **Fig. 1.** Schematic diagram of the pyrolysis-catalysis process of waste plastics.

162

163 2.3 Catalyst characterization

164 Crystal structure and species identification of the fresh catalysts were determined
165 by a X-ray diffraction (XRD) analyzer (X'Pert PRO, PANalytical B.V., Netherlands),
166 with a scanning step of 0.026° in the 2θ range from 5° to 85°. Peaks were identified
167 using High Score Plus software package. Temperature programmed reduction (TPR)

168 was also performed to characterize the fresh catalyst in a Shimadzu thermo
169 gravimetric analyzer (TGA). Approximately 30 mg of catalyst sample was preheated
170 to 150 °C at a heating rate of 20 °C min⁻¹ and held for 30 min in reduction
171 atmosphere (5 % H₂ / 95 % N₂), and then heated to 900 °C at 10 °C min⁻¹. The BET
172 surface area of the five Ni/Fe catalysts were calculated from N₂ adsorption and
173 desorption isotherms on an automatic adsorption equipment (ASAP2020,
174 Micromeritics, USA) operating at 77K.

175 The morphologies of CNTs were obtained using a scanning electron microscopy
176 (SEM) operating at 20 kV (JSM-5610LV, JEOL, Japan), and transmission electron
177 microscope (TEM) observation was also carried out on a FEI Tecnai TF20. The
178 thermal stability of carbon deposited on the catalysts was determined with
179 temperature-programmed oxidation (TPO) in a TGA (PerkinElmer Instruments, USA).
180 A total of 10 mg of the reacted catalyst was heated from room temperature to 800 °C
181 in air (100 ml min⁻¹) with a heating rate of 10 °C min⁻¹ and a holding time of 10 min
182 at 800 °C. Raman spectroscopy of deposited carbon was carried out to determine the
183 graphitic quality. And the spectrograms were obtained using a LabRAM HR800
184 (Horiba JobinYvon, Japan) Raman spectrometer at a wavelength of 532 nm with
185 Raman shift from 200 to 3500 cm⁻¹.

186

187 2.4 Analysis methods

188 Concentrations of the gases collected in the sample bag were obtained from gas
189 chromatography, and then the mass of each gas could be calculated based on the

190 concentrations and flow rate of carrier gas. Carbon deposition (solid) production was
191 determined as the mass difference between fresh and reacted catalyst. The liquid yield
192 of each experiment was obtained from the weight difference of the condenser before
193 and after the experimental test. The total gas, liquid and carbon deposition yields were
194 calculated by each product in relation to the total weight of waste plastics. Mass
195 balance was then obtained based on the sum of gas, liquid and solid yield to check the
196 reliability of each experiment. The mass balance in the presence of catalyst showed
197 good results, ranging from 95.7 to 101.4 wt.%, and a standard deviation of 0.22
198 vol. % of gas content was obtained for the repeated experiments. In order to better
199 present the hydrogen conversion from plastic, H₂ yield was defined as the mass of H₂
200 in the product gas divided by the theoretical H content in the feedstock according to
201 the ultimate analysis.

202

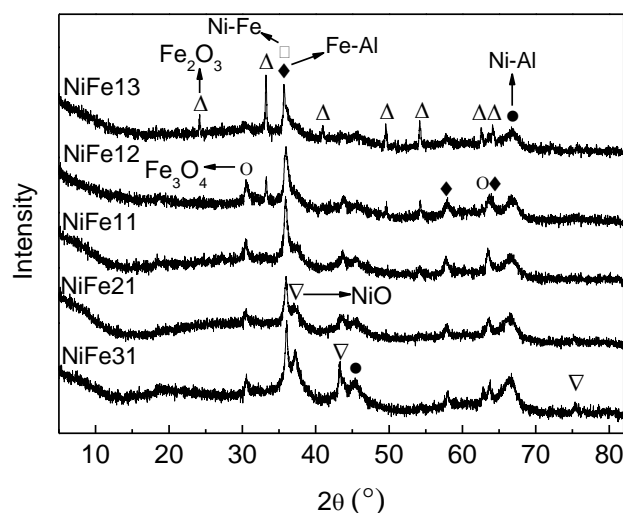
203 **3. Results and discussion**

204 3.1 Characterization of fresh catalyst

205 BET surface area of the fresh catalysts was 112.71, 109.72, 111.68, 106.90,
206 104.07 m² g⁻¹ for the catalyst NiFe13, NiFe12, NiFe11, NiFe21, NiFe31 respectively,
207 and the BJH average pore diameter was much similar in the range of 50 to 58 Å. It
208 seems these five catalysts were prepared with similar structure properties. The
209 crystalline structure of the fresh prepared Ni-Fe catalysts was shown in Fig. 2. There
210 are notable differences of crystal composition between catalysts with different Ni to
211 Fe ratio. Iron was observed with different oxidation state. The diffraction peak of

212 Fe_2O_3 was obviously detected with NiFe13. Both of Ni-Al and Fe-Al spinel were
213 observed, indicating the interaction between active metals and support, it is a key
214 factor for CNT production [24]. For NiFe12, the intensity of Fe_2O_3 was weak while
215 more Fe_3O_4 with a relatively lower valence state of Fe was found. And at higher ratio
216 of Ni to Fe, the peak of Fe_2O_3 can hardly be detected. It seems that the exiting of Ni
217 lead to part reduction of ferric iron, which might influence the reduction or cracking
218 ability of catalyst.

219

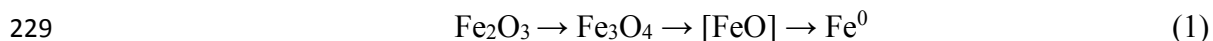


220

221 **Fig. 2.** X-ray diffraction profiles of the fresh Ni-Fe catalysts.

222

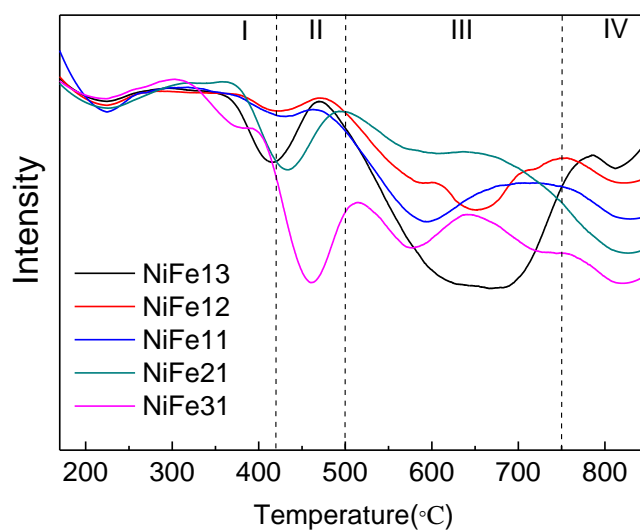
223 The reduction of Ni-Fe bimetallic catalysts is complex and presents in a number
224 of asymmetric stages (Fig.3). TPR results of NiFe13 show a peak around 400 °C in
225 addition to a broader peak from 500 to 750 °C and a peak higher than 750 °C. It
226 suggests that more than two metal species contributes to the reduction of NiFe13.
227 According to Al-Dossary et al. [32], the reduction of Fe_2O_3 undergoes two or even
228 three steps with the following sequence and occur in specified temperatures:



230 The first step was reported corresponding to the reduction of hematite into
231 magnetite, it mainly happens at around 400 °C. Further, it is reduced into [FeO]
232 (wustite, unstable) and metallic Fe occur at high temperatures and they always coexist,
233 which means it may produce some asymmetric and overlapped peaks [24, 32]. And
234 reduction kinetics change from chemical to diffusion controlling mechanism because
235 of high metal loading always lead to a higher reduction peak [33]. In order to classify
236 the reduction process clearly, four stages of reduction are indicated in Fig. 3.
237 Therefore, in this work, H₂ consumption peak observed at stage I belongs to the
238 reduction of Fe₂O₃ into Fe₃O₄, while the H₂ consumption at stage III was caused by
239 the subsequent reduction of Fe₃O₄ into FeO or Fe. For the NiFe12 and NiFe11, the
240 tiny peak at lower temperature suggests that the catalyst is not easy to be reduced,
241 indicating a strong interaction between metal and support. This is consistent with the
242 XRD results (Fig. 2) that Ni and Fe display a co-spinel state with support, and less
243 Fe₂O₃ or NiO was found. A peak at stage II can be seen for Ni-Fe bimetallic catalysts
244 at higher Ni to Fe ratio, and it attributes to the reduction of free NiO which interacts
245 weakly to γ-Al₂O₃ [34]. In addition, the peak intensity turns higher for NiFe31, and
246 results are consistent with the XRD results that more NiO sites are detected at high Ni
247 loading. NiFe31 also presents an obvious peak from 550 to 600 °C, which is related to
248 the reduction of NiO with high interaction with support according to [35]. All the five
249 catalysts show a reduction peak above 750 °C (stage IV), which is associated to a
250 spinel-metal phase where Ni or Fe has migrated into the support Al₂O₃ and is hardly

251 to be reduced [36]. In addition, as the hydrogen consumption of this metal-spinel
252 increased with the rising Ni to Fe ratio and it can be seen a larger proportion of Ni in
253 case of Ni-Al spinel than Fe in the Fe-Al spinel from TPR results, the overall
254 interaction between metal oxides and Al₂O₃ was enhanced with the rising Ni to Fe
255 ratio.

256



257

258 **Fig. 3.** Temperature programmed reduction profiles of the fresh Ni-Fe catalysts.

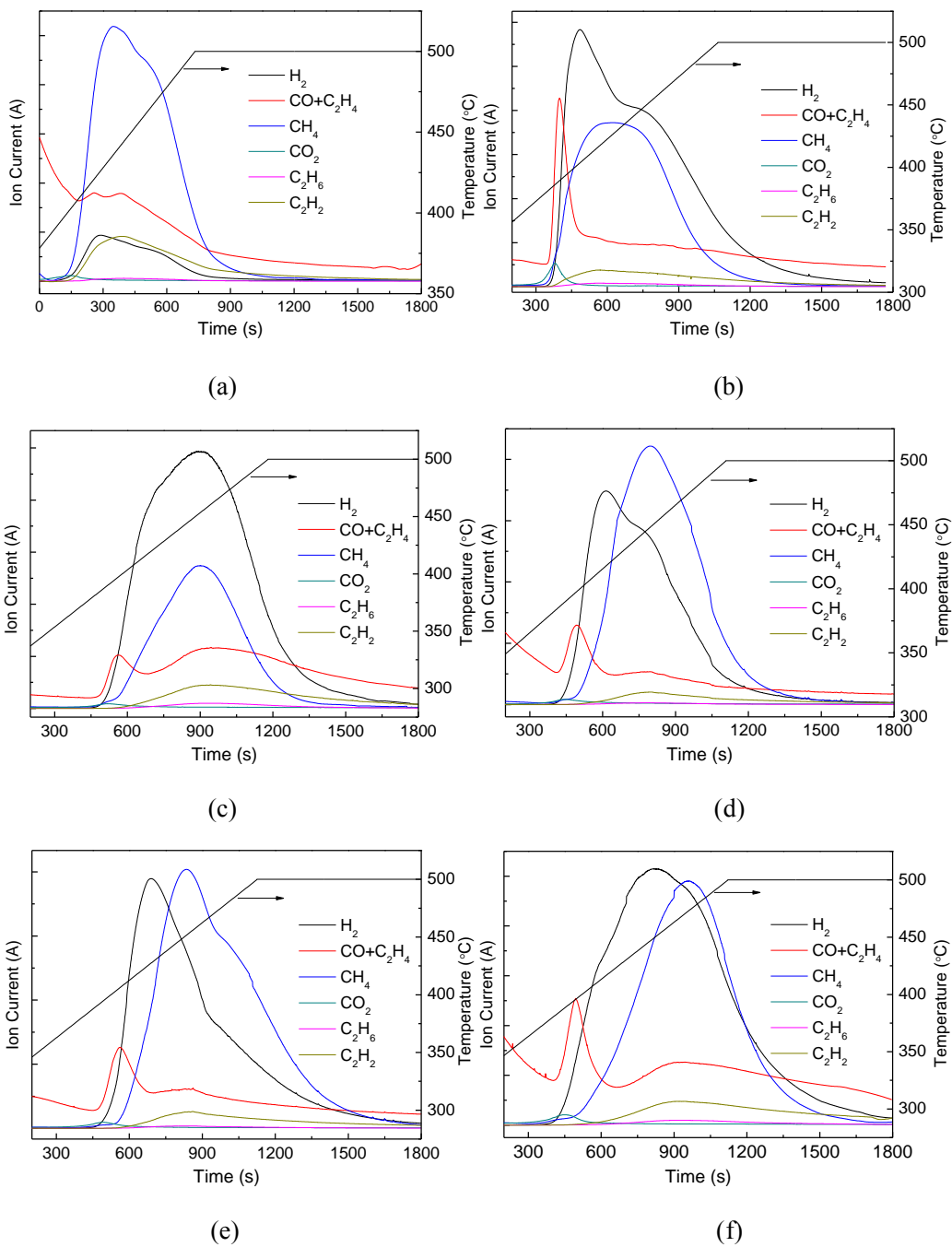
259

260 3.2 Gas releasing property of catalytic pyrolysis of waste plastics

261 For each experiment, less than 0.001g of pyrolysis char (~0.1 wt.%) was left for
262 each experiment (the balance has 1 mg readability), indicating that the plastics were
263 almost converted into vapours completely. Information about product evolution and
264 distribution can be obtained by means of mass spectrometer analysis. Ion-current
265 changes versus time during pyrolysis-catalytic process of plastics with/without
266 catalysts are shown in Fig. 4, and real-time temperature for each trial was also plotted.
267 As the oxygen content of plastics was very limited and oxygenic groups exist in side

268 chain of polymer, it is suggested that oxygen-contained compounds like CO and CO₂
269 are easily released at the beginning of the reaction. In that sense, for the signal of 28
270 a.m.u, which is the superposition of C₂H₄ and CO, the first peak was due to the
271 evolution of CO and the second was for the C₂H₄. It can be seen that gas from only
272 thermal cracking of plastic wastes (the no catalyst trial in Fig.4 (a)) mainly consist of
273 CH₄, C₂H₄. While CH₄ and C₂H₄ have been reported as good carbon sources for the
274 catalytic reaction for the production of CNTs [37], it is effective to use the Ni-Fe
275 catalyst for the following carbon formation reactions. When Ni-Fe catalysts were
276 applied, more H₂ was produced, with the maximum value achieved in the range of
277 430 to 450 °C. However, as the H₂ maximum peak without catalyst was around
278 420 °C, it seems that the gas release when using catalysts was delayed slightly. It may
279 due to the fact that more complexed reactions happened like catalyst redox and carbon
280 deposition. The ion intensity of C₂H₄ was considerably weak during the whole
281 catalysis process and it can be identified from the overlapped peak. It can be seen
282 NiFe12 and NiFe13 have higher H₂ selectivity than other catalysts as the plotted line
283 of H₂ was much higher than that of other gases. Gas emissions are similar at higher
284 ratio of Ni to Fe. The gas was released in the following order: CO_x (x=1, 2), H₂, C_xH_y
285 (including CH₄, C₂H₄, C₂H₂ and other hydrocarbons).

286



287

288

289

290

291

292

293 **Fig. 4.** Gas releasing behaviours during the pyrolysis-catalysis process of waste plastics. (a) no

294 catalyst, (b) NiFe13, (c) NiFe12, (d) NiFe11, (e) NiFe21, (f) NiFe31.

295

296 In order to compare these five catalysts in terms of different products quantities,

297 the gas yield, gas composition, solid yield as well as mass balance are summarized in

298 Table 1. Pyrolysis of waste plastics resulted in 50.51 wt.% gas yield, 2.2 wt.% carbon

299 deposits and 11.42 % hydrogen yield without catalyst (sand was used in place of
300 catalyst). The mass balance was 80.51 wt.% in the absence of catalyst. The low mass
301 balance may due to the inadequate decomposition of pyrolysis vapours that condensed
302 on the walls of reactor or converted to hydrocarbon gases which were hard to be
303 collected. H₂ yield was significantly increased using Ni-Fe bimetallic catalysts, and
304 reached maximum value of 61.17 % (84.72 mg g⁻¹ plastic) in the presence of NiFe13
305 catalyst. The lowest H₂ yield of 48.92 % was obtained with NiFe21 among all the
306 catalytic experiments. Regarding the total gas yield, catalysts with higher Ni to Fe
307 ratio showed relatively higher activity for total gas production than NiFe13 and
308 NiFe12, while the trend was opposite for the yield of carbon deposition. The carbon
309 deposition using NiFe13 was 50.9 wt.%, which was higher than that of NiFe11,
310 NiFe21 or NiFe31 (about 45 wt.%). It appears that NiFe13 and NiFe12, which contain
311 more Fe species, are more favorable for carbon deposits, than those catalysts with Ni
312 to Fe ratio higher than 1. It may due to the fact that the interaction between
313 metal-support of NiFe13 is moderately weak (from TPR results), and result in a high
314 yield of carbons [38]. This result agrees well with Acomb et al. [24], who found
315 Fe/Al₂O₃ generated a higher yield of carbon deposits than Ni/Al₂O₃ during
316 pyrolysis-catalytic process of low density polyethylene.

317 Table 1 also shows the volumetric content of gases. The controlled trial without
318 catalyst generated the highest amount of CH₄ and C₂H₄, with a content of 49.36
319 vol. % and 19.81 vol.%, respectively. And the content of CH₄ was twice of H₂, which
320 was consistent with the releasing trend observed in Fig. 4. The introduced five Ni-Fe

321 catalysts reduced hydrocarbon gases and accordingly increased H₂ content as a result
 322 of the catalytic cracking reactions (Reaction (2)). As more C was converted into solid
 323 state instead of gaseous product with the catalytic cracking reactions, hence the lower
 324 gas yield was observed with catalysts adding. The highest (73.93 vol.%) content of H₂
 325 was observed over NiFe13 catalyst, followed by NiFe12 and NiFe31, with the H₂
 326 content of 73.59 vol.% and 69.98 vol.%, respectively. It suggested the highest
 327 cracking ability of NiFe13, which was attribute to the presence of many reducible
 328 metal oxides observed from XRD (Fig. 2) and TPR (Fig. 3) results. NiFe11 and
 329 NiFe21 produced the relatively lower hydrogen content (around 64 vol.%) and higher
 330 CH₄ content (around 27 vol.%) among five Ni-Fe catalysts, which was also found in
 331 Fig. 4.



334 **Table 1**

335 Mass balance and gas production with different Ni-Fe catalysts.

	No catalyst ¹	NiFe13	NiFe12	NiFe11	NiFe21	NiFe31
H ₂ yield (%)	11.42	61.17	56.15	49.85	48.92	52.30
Gas yield (wt. %)	50.51	39.48	38.01	43.24	43.87	39.64
Carbon deposits (wt. %)	2.2	50.9	49.9	45.8	45.1	45.8
Liquid yield (wt.%)	27.8	8.8	13.5	7.1	9.9	10.3
Mass balance (%)	80.51	99.18	101.41	96.14	98.87	95.74
<i>Gas composition (vol. %)</i>						
H ₂	24.74	73.93	73.59	64.81	63.84	69.98
CO	2.98	3.90	3.74	4.19	3.76	4.37
CH ₄	49.36	16.77	15.12	26.40	27.16	19.15
CO ₂	0.67	0.62	0.64	0.77	0.65	0.76
C ₂ H ₄	19.81	3.43	4.88	3.12	3.60	4.15
C ₂ H ₆	2.24	1.30	1.97	0.63	0.92	1.56
C ₂ H ₂	0.20	0.04	0.05	0.08	0.07	0.04

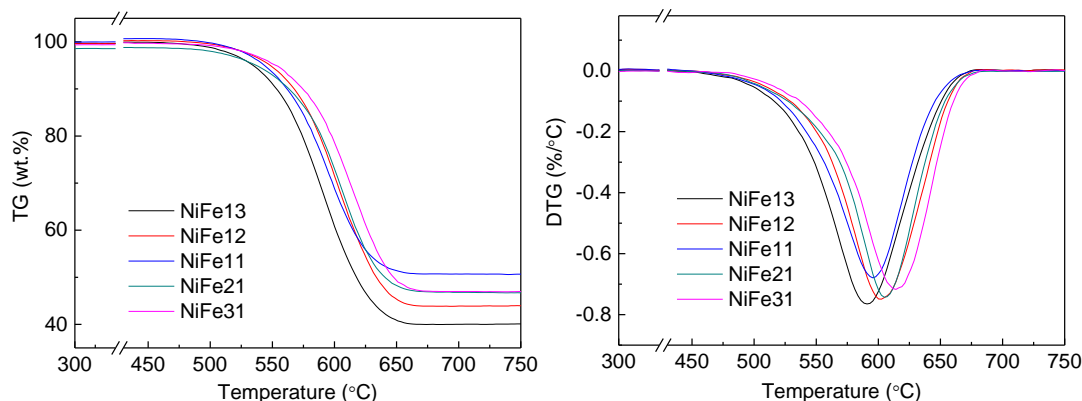
336 1: $T_1=500\text{ }^\circ\text{C}$, $T_2=800\text{ }^\circ\text{C}$, 0.5g silica sand.

337

338 3.3 Carbon nanotubes production

339 The oxidation properties of carbon nanomaterial obtained from the surface of
340 used catalyst samples were studied by temperature-programmed oxidation (TPO) as
341 shown in Fig. 5. According to the loss weight ratio of catalysts after oxidation, the
342 metal residues increased from 40 wt.% to 52 wt.% when Ni to Fe ratio increased from
343 1:3 to 3:1, suggesting a lower amount of metal-assisted carbon growth with more Ni
344 loading. It is consistent with the previous carbon yield results (Table 2) that NiFe13
345 catalysts produced the higher carbon deposits. The derivative TPO plots show that
346 most of the carbons were oxidized after $550\text{ }^\circ\text{C}$. Acomb et al [39] defined two types of
347 carbon with oxidation temperature in his work, where a lower temperature of TPO
348 peak from $350\text{ to }450\text{ }^\circ\text{C}$ was related to amorphous carbons and a higher temperature
349 between $500\text{ and }700\text{ }^\circ\text{C}$ was associated to the filamentous carbons. Yang et al. [22]
350 assigned the weight loss at $500\text{ }^\circ\text{C}$ to the amorphous carbon, and the oxidation at $600\text{ to }700$
351 $^\circ\text{C}$ to the multi-walled CNTs. As such, most of carbons formed in this study were
352 filamentous carbons. The carbon deposited on catalyst became less reactive when Ni
353 to Fe molar ratio increased, as the oxidation peak from DTG plots moved to higher
354 temperature with Ni content increased. It indicates that Ni composition in the catalyst
355 enhanced the thermal stability and graphitization of formed carbons. Sivakumar et al.
356 [40] synthesized Ni and Fe catalysts on active carbon for multi-walled carbon
357 nanotubes production from methane, and reported that CNTs formed on Ni exhibited
358 higher thermal stability than Fe.

359



360

361

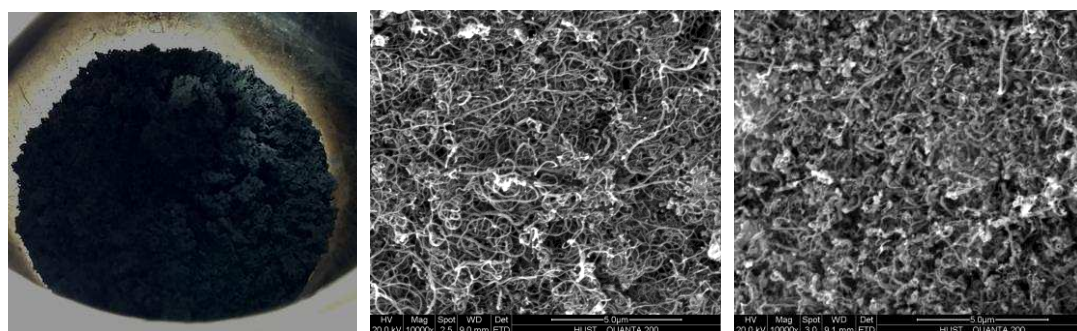
Fig. 5. Temperature program oxidation (TPO) of reacted catalysts.

362

363 The carbon residues obtained exhibited very fluffy solid particles (Fig. 6(a)),
364 accumulating a layer with thickness in the range of 10 to 15 mm (the catalyst layer
365 before reaction was 4mm). Fig. 6 also shows the SEM morphology of the synthesized
366 nanomaterials produced with five different catalysts. The filamentous type of carbon
367 could be clearly observed, and only a little proportion of disordered or amorphous
368 carbon were found, which was also suggested by TPO results.

369 The TEM images shown in Fig. 7 further confirmed that the carbon
370 nanomaterials winded on the surface of catalysts were carbon nanotubes with a
371 tubular-like form. These tubes have outer diameters ranging from 10 to 40 nm with
372 wall thicknesses from 3 to 10 nm. And the length can be up to a few micrometres (at
373 lower magnifications). Encapsulated catalyst nanoparticles can be seen in the middle
374 or at the top of the tubes, while the tube wall extended and coated on the surface of
375 the catalyst particle, forming a closed shell. Two different growth mode of carbon
376 nanotubes have been mentioned according to the metal position [41]. It appears the tip

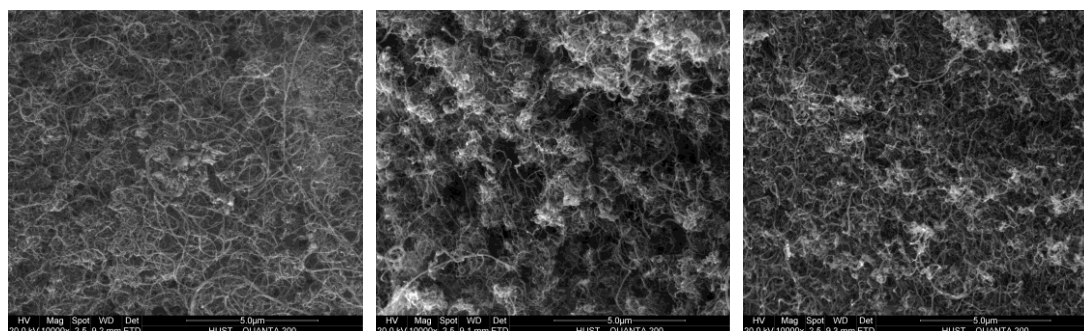
377 growth mechanism of CNTs formation was deduced during the catalysis-pyrolysis of
378 plastic wastes in this work. Besides, it can be seen that the diameters of carbon
379 nanotubes are approximately equal to the size of catalyst particles encapsulated in it.
380 It is indicated that the morphology of CNTs is related to the particle size of the
381 catalyst used [42]. And a strong metal-support interaction always lead to well
382 dispersed small catalyst particles [43]. From both SEM and TEM images, the CNTs
383 formed on NiFe21 and NiFe31 were found much thinner than those on NiFe13 and
384 NiFe12, simultaneously the stronger interaction between metal oxides and support
385 was observed at higher Ni to Fe ratio based TPR results. Similar results were also
386 found that, a narrower diameter of filamentous carbon was inclined to be observed
387 with a stronger metal-support interaction of catalyst [44]. In addition, more
388 homogeneous and longer nanotubes were seen in the NiFe31 catalyzed specimen, as
389 shown in Fig. 7(e).



390
391 (a)

(b)

(c)



392

393

(d)

(e)

(f)

394

Fig. 6. Carbon residues after reaction (observation with naked eye) (a) and SEM analysis of

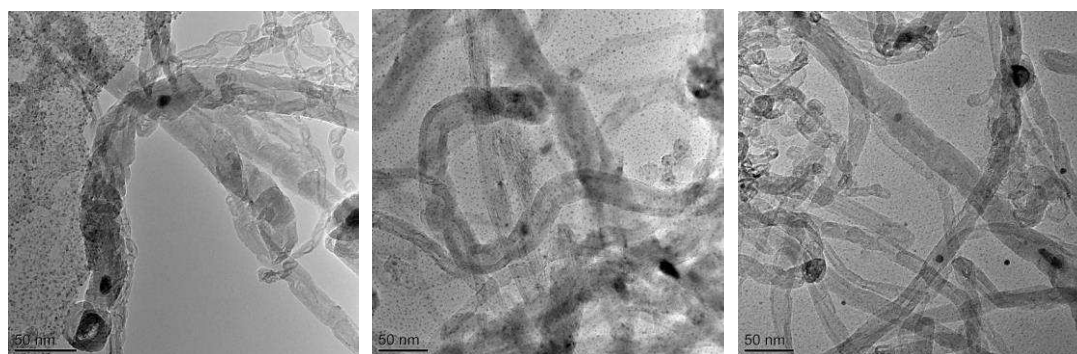
395

reacted catalysts with different Ni to Fe mole ratio (b) NiFe13, (c) NiFe12, (d) NiFe11, (e)

396

NiFe21, (f) NiFe31.

397



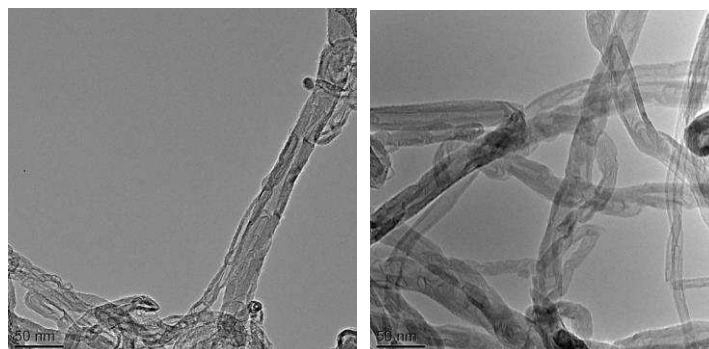
398

(a)

(b)

(c)

399



400

(d)

(e)

401

402

Fig. 7. TEM analysis of reacted catalysts with different Ni to Fe mole ratio. (a) NiFe13, (b)

403

NiFe12, (c) NiFe11, (d) NiFe21, (e) NiFe31.

404

405

Raman analysis (Fig. 8) was performed to evaluate the structure, crystallinity and

406

graphitization degree of carbons formed over Ni-Fe catalysts during the

407

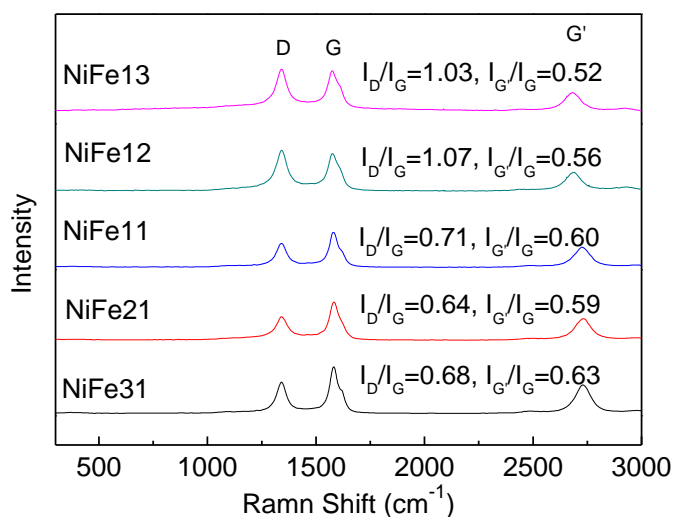
pyrolysis-catalytic process. The D band around wavelength of 1350 cm^{-1} is ascribed to

408 amorphous or disordered carbon, while the G band at around 1580 cm^{-1} is caused by
409 tangential vibration of the ordered graphite carbon atoms [45]. The peak intensity
410 ratio of I_D/I_G and $I_{G'}/I_G$ are used to estimate the defects and graphitization degree of
411 carbon deposits. It can be seen that all of the current catalysts have the I_D/I_G ratio
412 between 0.64 and 1.03, and the $I_{G'}/I_G$ ratio from 0.52 to 0.63, comparably with the
413 CNTs in commercial application or with other literatures [46]. In addition, I_D/I_G ratio
414 decreased and $I_{G'}/I_G$ increased at higher ratios of the Ni to Fe catalysts. It appears
415 NiFe21 and NiFe31 have fewer defects than other three catalysts, similar to results
416 observed by TEM. As thermal stability also increased with the increasing ratio of Ni
417 to Fe (from TPO analysis), indicating the thermal stability of carbon is related to the
418 carbon defects (from Raman analysis). Tian et al. [47] also ascribed the good
419 performance of CNTs in heat treatment to the clean and smooth wall surfaces. As for
420 the Ni-Fe catalyst investigated in this work, it can be seen that Ni improves the purity
421 and graphitization degree of carbon nonmaterial.

422 In order to make a comparison between our results and those of literatures, yields
423 of hydrogen and carbon nanotubes using different waste plastics and Ni-Fe based
424 catalysts are gathered in Table 2. Details of morphology and quality of CNTs are also
425 present. It can be seen, compared with other catalysts with similar operation
426 conditions (catalysis temperature: 750 to 800, no steam feeding, fixed bed reactor),
427 bimetallic Ni-Fe catalysts exhibited better performance for simultaneous H_2 and CNTs
428 production from waste polymers. It may because C-C bond cleavage and cracking
429 activity of catalyst were enhanced by using bimetallic catalysts and therefore

430 increasing H₂ and carbon yields [27]. The relatively lower I_D/I_G also implies better
 431 morphology and purity of carbons obtained over Ni-Fe catalyst.

432



433

434 **Fig. 8.** Raman analysis of the five reacted Ni-Fe catalysts.

435

436 **Table 2**

437 Comparison of H₂, CNTs yield and Raman indicators between our results and those reported in
 438 literatures.

Material	Catalyst	H ₂ yield (g/100g sample)	H ₂ content (Vol. %)	Carbon (g/100g sample)	I _D /I _G	Source
Mixed plastics	NiFe31/Al ₂ O ₃	7.24	69.98	46	0.68	this work
LDPE	Ni/ Al ₂ O ₃	3.30	58.30	52	0.59	[48]
PS	Ni/ Al ₂ O ₃	2.70	77.20	25	0.93	[48]
PP and PE mixture	H-Ni/ Al ₂ O ₃	5.72	36.13	31	—	[22]
LDPE	Fe/ Al ₂ O ₃	3.90	51.00	27	0.51	[39]
Waste tires	Fe/ Al ₂ O ₃	1.50	33.12	38	0.89	[21]
Mixed plastics	Ni-Mn-Al	12.2	75.6	46	0.9	[10]

439

440 4. Conclusions

441 H₂-rich syngas and high yield of carbon nanotubes were produced with bimetallic

442 Ni-Fe catalysts from real-word waste plastics. The effect of different Ni to Fe molar

443 ratios during catalyst preparation on the gas product and properties of carbon deposits
444 was studied. The maximum H₂ yield of 8.47 g g⁻¹ plastic and H₂ content of 73.93
445 vol.% were obtained with the NiFe13 catalyst having the highest fraction of Fe. TGA,
446 TEM and Raman analysis have revealed that highly graphitized carbon nanotubes
447 were obtained over all Ni-Fe catalysts. The yield of deposited carbon was related to
448 the metal-support interaction, and higher yield of carbon was obtained for the
449 catalysts with higher Fe loading. However carbon nanotubes with narrower diameters
450 and uniform distributions were grown with higher Ni ratio. The presence of Ni
451 enhanced the thermal stability of the produced carbon products with less carbon
452 defects and higher graphitization degree of carbon, and a higher thermal stability of
453 filamentous carbon over the NiFe31 catalyst was obtained. There is potential
454 flexibility of the bimetallic catalyst for this process, where by adjusting the molar
455 ratio of Ni to Fe the final products can be turned for the production of hydrogen or
456 carbon nanotubes with higher purity.

457

458 **Acknowledgements**

459 The authors would like to thank the financial support from the National Natural
460 Science Foundation of China (51622604 and 51376076) and the China Postdoctoral
461 Science Foundation (2016M602293). The experiment was also assisted by Analytical
462 and Testing Center in Huazhong University of Science & Technology
463 (<http://atc.hust.edu.cn>), Wuhan 430074 China.

464

465

466 **References**

- 467 [1] Gu B, Jiang S, Wang H, Wang Z, Jia R, Yang J, et al. Characterization, quantification and
468 management of China's municipal solid waste in spatiotemporal distributions: A review.
469 Waste Management 2016;**61**:67-77.
- 470 [2] PlasticsEurope. Plastics - the Facts 2016. 2016.
- 471 [3] Sharuddin S D A, Abnisa F, Daud W M A W, Aroua M K. A review on pyrolysis of plastic wastes.
472 Energy Conversion and Management 2016;**115**:308-326.
- 473 [4] Miandad R, Barakat M, Aburiazza A S, Rehan M, Nizami A. Catalytic pyrolysis of plastic waste:
474 a review. Process Safety and Environmental Protection 2016;**102**:822-838.
- 475 [5] Lopez G, Artetxe M, Amutio M, Bilbao J, Olazar M. Thermochemical routes for the valorization
476 of waste polyolefinic plastics to produce fuels and chemicals. A review. Renewable and
477 Sustainable Energy Reviews 2017;**73**:346-368.
- 478 [6] Williams P T, Williams E A. Fluidised bed pyrolysis of low density polyethylene to produce
479 petrochemical feedstock. Journal of Analytical and Applied Pyrolysis 1999;**51**:107-126.
- 480 [7] Ratnasari D K, Nahil M A, Williams P T. Catalytic pyrolysis of waste plastics using staged
481 catalysis for production of gasoline range hydrocarbon oils. Journal of Analytical and Applied
482 Pyrolysis 2017;**124**:631-637.
- 483 [8] Dou B, Wang K, Jiang B, Song Y, Zhang C, Chen H, et al. Fluidized-bed gasification combined
484 continuous sorption-enhanced steam reforming system to continuous hydrogen production
485 from waste plastic. International Journal of Hydrogen Energy 2016;**41**:3803-3810.
- 486 [9] Arregi A, Amutio M, Lopez G, Artetxe M, Alvarez J, Bilbao J, et al. Hydrogen-rich gas
487 production by continuous pyrolysis and in-line catalytic reforming of pine wood waste and
488 HDPE mixtures. Energy Conversion and Management 2017;**136**:192-201.
- 489 [10] Wu C, Nahil M A, Miskolczi N, Huang J, Williams P T. Processing Real-World Waste Plastics by
490 Pyrolysis-Reforming for Hydrogen and High-Value Carbon Nanotubes. Environmental science
491 & technology 2013;**48**:819-826.
- 492 [11] Zhang Y, Williams P T. Carbon nanotubes and hydrogen production from the pyrolysis catalysis
493 or catalytic-steam reforming of waste tyres. Journal of Analytical and Applied Pyrolysis
494 2016;**122**:490-501.
- 495 [12] Wu C, Nahil M A, Miskolczi N, Huang J, Williams P T. Production and application of carbon
496 nanotubes, as a co-product of hydrogen from the pyrolysis-catalytic reforming of waste
497 plastic. Process Safety and Environmental Protection 2016;**103, Part A**:107-114.
- 498 [13] Borsodi N, Szentés A, Miskolczi N, Wu C, Liu X. Carbon nanotubes synthesized from gaseous
499 products of waste polymer pyrolysis and their application. Journal of Analytical and Applied
500 Pyrolysis 2016;**120**:304-313.
- 501 [14] Iijima S. Helical microtubules of graphitic carbon. Nature 1991.
- 502 [15] Baughman R H, Zakhidov A A, de Heer W A. Carbon nanotubes--the route toward applications.
503 Science 2002;**297**:787-792.
- 504 [16] De Volder M F, Tawfick S H, Baughman R H, Hart A J. Carbon nanotubes: present and future
505 commercial applications. Science 2013;**339**:535-539.
- 506 [17] Shah K A, Tali B A. Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A
507 review on carbon sources, catalysts and substrates. Materials Science in Semiconductor
508 Processing 2016;**41**:67-82.
- 509 [18] Uddin M N, Daud W W, Abbas H F. Co-production of hydrogen and carbon nanofibers from

- 510 methane decomposition over zeolite Y supported Ni catalysts. *Energy Conversion and*
511 *Management* 2015;**90**:218-229.
- 512 [19] Wu C F, Wang Z C, Huang J, Williams P T. Pyrolysis/gasification of cellulose, hemicellulose and
513 lignin for hydrogen production in the presence of various nickel-based catalysts. *Fuel*
514 2013;**106**:697-706.
- 515 [20] Yao D, Hu Q, Wang D, Yang H, Wu C, Wang X, et al. Hydrogen production from biomass
516 gasification using biochar as a catalyst/support. *Bioresource Technology* 2016;**216**:159-164.
- 517 [21] Zhang Y, Wu C, Nahil A, Williams P T. Pyrolysis-Catalytic Steam Reforming/Gasification of
518 Waste Tires for Production of Carbon Nanotubes and Hydrogen. *Energy & Fuels* 2015.
- 519 [22] Yang R-X, Chuang K-H, Wey M-Y. Effects of nickel species on Ni/Al₂O₃ catalysts in CNTs and
520 hydrogen production by waste plastics gasification: Bench-scale and pilot-scale tests. *Energy*
521 *& Fuels* 2015.
- 522 [23] Pudukudy M, Yaakob Z, Takriff M S. Methane decomposition into CO_x free hydrogen and
523 multiwalled carbon nanotubes over ceria, zirconia and lanthana supported nickel catalysts
524 prepared via a facile solid state citrate fusion method. *Energy Conversion and Management*
525 2016;**126**:302-315.
- 526 [24] Acomb J C, Wu C, Williams P T. The use of different metal catalysts for the simultaneous
527 production of carbon nanotubes and hydrogen from pyrolysis of plastic feedstocks. *Applied*
528 *Catalysis B: Environmental* 2016;**180**:497-510.
- 529 [25] Popovska N, Danova K, Jipa I, Zenneck U. Catalytic growth of carbon nanotubes on zeolite
530 supported iron, ruthenium and iron/ruthenium nanoparticles by chemical vapor deposition in
531 a fluidized bed reactor. *Powder Technology* 2011;**207**:17-25.
- 532 [26] Cartwright R, Esconjauregui S, Hardeman D, Bhardwaj S, Weatherup R, Guo Y, et al. Low
533 temperature growth of carbon nanotubes on tetrahedral amorphous carbon using Fe–Cu
534 catalyst. *Carbon* 2015;**81**:639-649.
- 535 [27] Kaya B, Irmak S, Hasanoğlu A, Erbatur O. Developing Pt based bimetallic and trimetallic carbon
536 supported catalysts for aqueous-phase reforming of biomass-derived compounds.
537 *International Journal of Hydrogen Energy* 2015;**40**:3849-3858.
- 538 [28] Shen Y, Zhao P, Shao Q, Takahashi F, Yoshikawa K. In situ catalytic conversion of tar using rice
539 husk char/ash supported nickel–iron catalysts for biomass pyrolytic gasification combined
540 with the mixing-simulation in fluidized-bed gasifier. *Applied Energy* 2015;**160**:808-819.
- 541 [29] Wei G, He F, Zhao Z, Huang Z, Zheng A, Zhao K, et al. Performance of Fe–Ni bimetallic oxygen
542 carriers for chemical looping gasification of biomass in a 10 kWth interconnected circulating
543 fluidized bed reactor. *International Journal of Hydrogen Energy* 2015;**40**:16021-16032.
- 544 [30] Shen W, Huggins F E, Shah N, Jacobs G, Wang Y, Shi X, et al. Novel Fe–Ni nanoparticle catalyst
545 for the production of CO- and CO₂-free H₂ and carbon nanotubes by dehydrogenation of
546 methane. *Applied Catalysis A: General* 2008;**351**:102-110.
- 547 [31] Yao D, Wu C, Yang H, Hu Q, Nahil M A, Chen H, et al. Hydrogen production from catalytic
548 reforming of the aqueous fraction of pyrolysis bio-oil with modified Ni–Al catalysts.
549 *International Journal of Hydrogen Energy* 2014;**39**:14642-14652.
- 550 [32] Al-Dossary M, Fierro J. Effect of high-temperature pre-reduction in Fischer–Tropsch synthesis
551 on Fe/ZrO₂ catalysts. *Applied Catalysis A: General* 2015;**499**:109-117.
- 552 [33] Sepúlveda R, Plunk A A, Dunand D C. Microstructure of Fe₂O₃ scaffolds created by
553 freeze-casting and sintering. *Materials Letters* 2015;**142**:56-59.

- 554 [34] de Freitas Silva T, Dias J A C, Maciel C G, Assaf J M. Ni/Al₂O₃ catalysts: effects of the
555 promoters Ce, La and Zr on the methane steam and oxidative reforming reactions. *Catalysis
556 Science & Technology* 2013;**3**:635-643.
- 557 [35] Alipour Z, Rezaei M, Meshkani F. Effects of support modifiers on the catalytic performance of
558 Ni/Al₂O₃ catalyst in CO₂ reforming of methane. *Fuel* 2014;**129**:197-203.
- 559 [36] Valle B, Aramburu B, Remiro A, Bilbao J, Gayubo A G. Effect of calcination/reduction
560 conditions of Ni/La₂O₃- α -Al₂O₃ catalyst on its activity and stability for hydrogen
561 production by steam reforming of raw bio-oil/ethanol. *Applied Catalysis B: Environmental*
562 2014;**147**:402-410.
- 563 [37] Gallego G S, Barrault J, Batiot-Dupeyrat C, Mondragón F. Production of hydrogen and MWCNTs
564 by methane decomposition over catalysts originated from LaNiO₃ perovskite. *Catalysis Today*
565 2010;**149**:365-371.
- 566 [38] Nahil M A, Wu C, Williams P T. Influence of metal addition to Ni-based catalysts for the
567 co-production of carbon nanotubes and hydrogen from the thermal processing of waste
568 polypropylene. *Fuel Processing Technology* 2015;**130**:46-53.
- 569 [39] Acomb J C, Wu C, Williams P T. Effect of growth temperature and feedstock: catalyst ratio on
570 the production of carbon nanotubes and hydrogen from the pyrolysis of waste plastics.
571 *Journal of Analytical and Applied Pyrolysis* 2015.
- 572 [40] Sivakumar V, Abdullah A Z, Mohamed A R, Chai S-P. Optimized parameters for carbon
573 nanotubes synthesis over Fe and Ni catalysts VIA methane CVD. *Rev. Adv. Mater. Sci*
574 2011;**27**:25-30.
- 575 [41] Huang S, Woodson M, Smalley R, Liu J. Growth mechanism of oriented long single walled
576 carbon nanotubes using "fast-heating" chemical vapor deposition process. *Nano Letters*
577 2004;**4**:1025-1028.
- 578 [42] Chung Y-H, Jou S. Carbon nanotubes from catalytic pyrolysis of polypropylene. *Materials
579 chemistry and physics* 2005;**92**:256-259.
- 580 [43] Cargnello M, Doan-Nguyen V V, Gordon T R, Diaz R E, Stach E A, Gorte R J, et al. Control of
581 metal nanocrystal size reveals metal-support interface role for ceria catalysts. *Science*
582 2013;**341**:771-773.
- 583 [44] Yeoh W-M, Lee K-Y, Chai S-P, Lee K-T, Mohamed A R. Effective synthesis of carbon nanotubes
584 via catalytic decomposition of methane: Influence of calcination temperature on
585 metal-support interaction of Co-Mo/MgO catalyst. *Journal of Physics and Chemistry of Solids*
586 2013;**74**:1553-1559.
- 587 [45] Gong J, Liu J, Wan D, Chen X, Wen X, Mijowska E, et al. Catalytic carbonization of
588 polypropylene by the combined catalysis of activated carbon with Ni₂O₃ into carbon
589 nanotubes and its mechanism. *Applied Catalysis A: General* 2012;**449**:112-120.
- 590 [46] Awadallah A E, Aboul-Enein A A, Aboul-Gheit A K. Effect of progressive Co loading on
591 commercial Co-Mo/Al₂O₃ catalyst for natural gas decomposition to CO_x-free hydrogen
592 production and carbon nanotubes. *Energy Conversion and Management* 2014;**77**:143-151.
- 593 [47] Tian F, Li H, Zhao N, He C. Catalyst effects of fabrication of carbon nanotubes synthesized by
594 chemical vapor deposition. *Materials chemistry and physics* 2009;**115**:493-495.
- 595 [48] Acomb J C, Wu C, Williams P T. Control of steam input to the pyrolysis-gasification of waste
596 plastics for improved production of hydrogen or carbon nanotubes. *Applied Catalysis B:
597 Environmental* 2014;**147**:571-584.