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The Combined Catalytic Action of Solid Acids with Nickel for the Transformation of Polypropylene into Carbon Nanotubes by Pyrolysis

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Abstract: The effects of both organically modified montmorillonite (OMMT) and Ni_2O_3 on the carbonization of polypropylene (PP) during pyrolysis were investigated. The results from TEM and Raman spectroscopy showed that the carbonized products of PP were mainly multiwalled carbon nanotubes (MWNTs). Surprisingly, a combination of OMMT and Ni_2O_3 led to high-yield formation of MWNTs. X-ray powder diffraction (XRD) and GC–MS were used to investigate the mechanism of this combination for the high-yield formation of MWNTs from PP. Brønsted acid sites were created in degraded OMMT layers by thermal decomposition of the modifiers. The resultant carbenium ions play an important role in the carbonization of PP and the formation of MWNTs. The degradation of PP was induced by the presence of carbenium ions to form predominantly products with lower carbon numbers that could be easily catalyzed by the nickel catalyst for the growth of MWNTs. Furthermore, carbenium ions are active intermediates that promote the growth of MWNTs from the degradation products with higher carbon numbers through hydride-transfer reactions. The XRD measurements showed that Ni_2O_3 was reduced into metallic nickel (Ni) in situ to afford the active sites for the growth of MWNTs.

Keywords: carbenium ions · catalysis · nanotubes · nickel · pyrolysis

Introduction

The total amount of plastic waste generated by our society is growing rapidly. Landfill is undesirable due to the low biodegradability of plastics, especially polyolefins, which are one of the main components of plastic waste. Therefore, the effective disposal of the waste, a serious environmental problem, is a research topic that needs to be explored. Waste can be thought of as a resource reservoir, this becomes significant when the shortage of resources is considered.[1] Incineration can be used to transfer the waste plastic into energy, however, the loss of potential chemical resources and the negative public acceptance has limited the application of this solution. Conversion of the used plastics into valuable chemicals or materials is an ideal alternative. Degradation of recycled polyolefins has been widely explored with regard to preparing hydrocarbons and fuel.[2] Catalytic degradation, which usually takes place in the presence of solid acids, operates at lower temperature than that of thermal degradation, and affords quality products that, however, are still a mixture of various components with different carbon numbers and different structures. Synthesis of carbon nanotubes (CNTs) from carbon materials is a new potential application for recycling polyolefins.

The range of new methods for the synthesis of CNTs since their discovery[3] is attractive, as CNTs possess unique properties and applications.[4] Catalytic decomposition of carbon containing feedstock is a promising method for the production of CNTs on a large scale.[5] Numerous carbon-containing chemicals, such as CH_4, C_2H_2, and C_6H_6, were used as carbon sources to produce CNTs through catalysis. Polymeric materials, such as polyolefins, have been explored as starting materials for the preparation of CNTs.[6] This offers the advantage of resource saving and environmental protection, as to sustain development and an increasing demand for petroleum, a large amount of virtually nondegradable polyolefins to be recycled replacing incineration and landfilling. A further advantage of carbonization is the release of hydrogen gas. However, recycling polymers as carbon sources leads to problems; the yield of conversion is

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low, because the temperature for pyrolysis of carbon sources to synthesize CNTs is higher than that for degradation of polymers, thus, most of the degradation products escape as gaseous components. Chung et al. reported the synthesis of multiwalled CNTs (MWNTs) from catalytic pyrolysis of polypropylene (PP) by iron nanoparticles, however, the conversion of PP was not provided.[6g] Furthermore, the mechanism is extremely complicated because degradation and carbonization take place simultaneously. The pathways of thermal or catalytic degradation[7] are different, the former is based on a free radical active intermediate and the latter is based on a carbenium ion as the active intermediate. Two kinds of degradation reaction can result in different degradation products, which can affect the carbonization behavior, the resulting yield, and structure of the CNTs. The match of carbon sources with catalyst is an important factor for the yield of CNTs.[8] Our previous results show that a PP mixture containing a supported nickel catalyst (S−Ni) and organically modified montmorillonite (OMMT) could be transformed into MWNTs with high yield through a combustion reaction.[9] We have shown that montmorillonite (MMT) that contains hydrogen protons (H−MMT) will form on MMT layers after the thermal decomposition of alkylammonium in OMMT. The thermal degradation of PP will then change into the catalytic degradation of PP as H−MMT begins to act as a degradation catalyst during pyrolysis. Therefore, in the presence of both OMMT and nickel catalyst, two kinds of catalytic reaction are involved during synthesis of MWNTs from PP, one being catalytic degradation of PP and the other carbonization of the degradation products. However, the chemical nature of the combination of OMMT and nickel catalyst for the formation of MWNTs needs to be further investigated, especially the effect of active intermediates, which is seldom reported. During preparation of this paper, we noticed a report from Reilly and Whitten,[10] in which free radical condensates were thought to act as an intermediate and reaction medium for the hydrocarbon-based chemical vapor deposition (CVD) production of CNTs. We were interested to see how the carbenium ions will influence the formation of MWNTs in the reaction system. By using PP as a model polymer, the combined catalysis of solid acid and nickel catalyst on formation of MWNTs during pyrolysis was investigated. We report whether and how the catalytic degradation reaction influences the carbonization during pyrolysis of PP due to existence of carbenium ions as active intermediates. Our motivation is to establish a basis for the transformation of used polyolefin into CNTs.

Results and Discussion

Carbonization behavior of PP/PPMA/OMMT/Ni_2O_3 mixture during one-pot pyrolysis: Based on our previous results,[9] the carbonization behavior of a PP/PPMA/OMMT/Ni_2O_3 = 80/10/5/5 (by weight)(PPMA=maleated polypropylene) mixture was investigated in a one-pot pyrolysis at 700 °C. A Ni_2O_3 compound was used instead of the S-Ni, combined with the OMMT. The charred residue was composed of fiber like char and MMT layers (Figure 1 a,b). After purifying, TEM observation showed that the purified fiber like char contained MWNTs (Figure 1 c). The yield of MWNTs was 44.8 wt % (Table 1). A detailed structure of a single tube of the purified MWNTs is given in an image of high-resolution transmission electron microscopy (HRTEM) (Figure 1d). The sidewall of the tube consists of graphite layers, which are not perfectly concentric. Raman spectroscopy was used to characterize the vibrational properties of the obtained MWNTs. There are two vibrational peaks on the Raman spectrum of the above sample (Figure 2). The peak at 1581 cm^{-1} (G-band) corresponds to an E_{2g} mode of hexagonal graphite and is related to the vibration of sp^2-bonded carbon atoms in a graphite layer, and the D-band at 1347 cm^{-1} is associated with vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite or glassy carbons. The results from thermogravi-

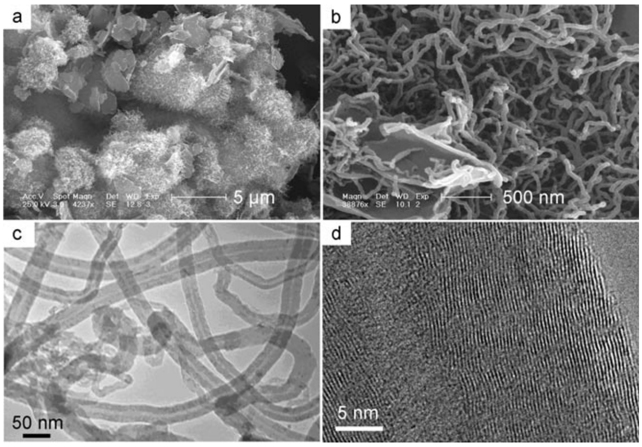


Figure 1. Microstructure of the char prepared from PP mixtures with 5 wt % of OMMT and 5 wt % of Ni_2O_3 by a one-pot pyrolysis. a) and b) FESEM micrographs of the obtained sample, c) TEM micrograph of the sample purified by HF and HNO_3, d) higher magnification TEM image of a typical MWNT.

Table 1. Effect of solid acids on the yield of MWNTs (at 700 °C).

Pyrolysis method	Solid acid	Yield of MWNTs [wt %][c]
one-pot[a]	blank	8.0
	Na−MMT	15.6
	OMMT	44.8
	NH_4−MMT	56.0
	Na−ZSM-5	10.9
	H−ZSM-5	42.0
two-stage[b]	blank	5.0
	OMMT	28.0

[a] PP/PPMA/inorganic solid/Ni_2O_3 = 80/10/5/5, and the "blank" sample of PP/PPMA/Ni_2O_3 = 80/10/5; these samples were pyrolyzed directly. [b] The degradation products of 95 parts PP/PPMA/OMMT = 80/10/5 or 90 parts PP/PPMA = 80/10 (for the "blank" sample) passed through 5 parts Ni_2O_3. [c] After purification by HNO_3 and HF.

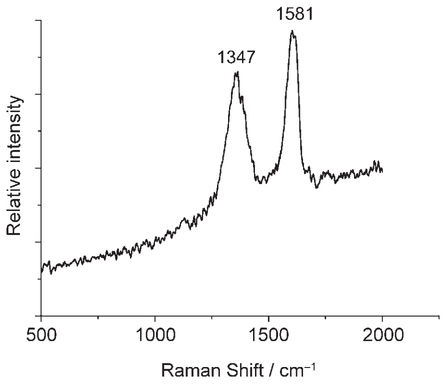


Figure 2. Raman spectra of the purified MWNTs from a PP/PPMA/OMMT/Ni_2O_3 = 80/10/5/5 (by weight) mixture.

metric analysis (TGA) showed that the maximum weight loss of the purified MWNTs occurred at 560 °C (Figure 3).

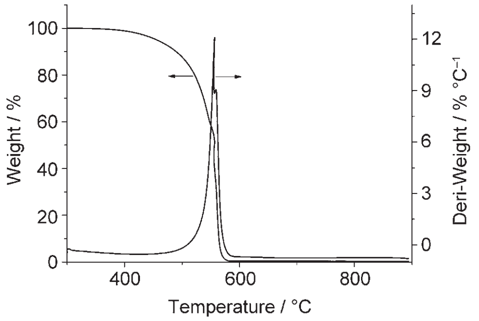


Figure 3. TGA weight-loss curves of the purified MWNTs from a PP/PPMA/OMMT/Ni_2O_3 = 80/10/5/5 (by weight) mixture.

A little decomposition occurs at temperatures below 500 °C, indicating that the MWNT sample is relative pure. The decomposition temperature of these MWNTs is slightly lower than that previously reported for MWNTs that had been synthesized by supercritical fluids and CVD.[11] The difference in decomposition temperature may be attributed to some disordered graphite or glassy carbons that exist in the sidewalls of MWNTs. This result is consistent with those of Raman spectroscopy and HRTEM.

Effects of Brønsted acid sites of solid acids on the yield of MWNTs from PP during one-pot pyrolysis: The effect of various solid acids in the PP matrix on the yield of MWNTs during one-pot pyrolysis at 700 °C is exhibited in Table 1. In the absence of solid acids, the carbonization of the PP/PPMA/Ni_2O_3 = 80/10/5 (by weight) mixture did not give a high yield of MWNTs. In contrast, in the presence of both OMMT and Ni_2O_3, the yield of MWNTs was increased to 44.8 wt %, which was similar to our previous results.[9] After Na^+–montmorillonite (Na–MMT) was modified by $NH_4^+Cl^-$ by ion exchange (NH_4–MMT), the PP/PPMA/NH_4–MMT/Ni_2O_3 = 80/10/5/5 (by weight) mixture gave a much higher yield of MWNTs (56.0 wt %, Table 1, NH_4–MMT). However, the combination of Na–MMT and Ni_2O_3 in a PP matrix afforded a yield of only 15.6 wt % under the same conditions (Table 1, Na–MMT). As the degree of dispersion of NH_4–MMT is similar to that of Na–MMT and not as good as that of OMMT, it should not contribute to the high-yield formation of the MWNTs. Other factors that strongly influence carbonization of PP catalyzed by Ni_2O_3 must exist.

It is known that the thermal decomposition of (alkyl)ammonium in the OMMT or NH_4–MMT will leave hydrogen protons on the MMT layers to form H–MMT.[12] The FTIR spectra of adsorbed pyridine after desorption at 150 °C on Na–MMT and H–MMTs from thermal decomposition of OMMT and NH_4–MMT provide an insight into the nature of the acid sites in these materials (Figure 4). Two bands at 1548 and 1441 cm^{-1}, which are characteristic of Brønsted and Lewis acid sites,[13] respectively, were observed for the H–MMTs. However, no such band at 1548 cm^{-1} was observed for the Na–MMT. This suggests that Brønsted acid sites on the H–MMTs are a key factor to the high-yield formation of MWNTs.

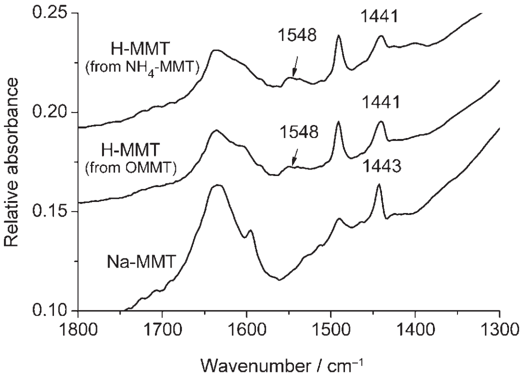


Figure 4. FTIR spectra of the adsorbed pyridine on Na–MMT and H–MMTs from OMMT and NH_4–MMT in the 1300–1800 cm^{-1} range after pyridine adsorption and then desorption at 150 °C.

To confirm the effect of Brønsted acid sites on the yield of MWNTs, we chose commercial catalysts H–ZSM-5 and NaOH modified H–ZSM-5 (Na–ZSM-5), respectively, together with Ni_2O_3, to form combined catalysts to catalyze the degradation of PP and then form MWNTs. The use of the solid acid H–ZSM-5 for the catalytic degradation of PP has previously been reported.[14] The yield of MWNTs obtained from the mixture of PP/PPMA/H–ZSM-5/Ni_2O_3 = 80/10/5/5 (by weight) in a one-pot pyrolysis was higher than that from the PP/PPMA/Na–ZSM-5/Ni_2O_3 = 80/10/5/5 (by weight) mixture (Table 1, H–ZSM-5 vs. Na–ZSM-5). It is well known that the use of acid-center catalysts in pyrolysis results in carbon deposits (amorphous carbon) during hydrocarbon decomposition.[15] The amorphous carbon is thought to grow simultaneously with the CNTs on the acid sites of the combined/nickel solid-acid catalyst, which would give rise to a considerable increase in the production of carbon deposits. However, the yield of carbon material from PP/PPMA/OMMT or PP/PPMA/H–ZSM-5 mixtures is less than 6 wt % after pyrolysis at the same conditions. The considerable increase in carbon deposits from solid acids did not occur. Thus, the high-yield formation of MWNTs from PP should mainly be attributed to the combined catalysis of Brønsted acid sites on the solid acids and Ni_2O_3.

The main use of Brønsted acid sites on the solid acids is to catalyze the degradation of PP. The activation energy of catalytic degradation is lower than that of thermal degradation.[7b] Thus, catalytic degradation occurs more readily than thermal degradation. The experimental results showed that the degradation products from catalytic degradation of PP by the OMMT precursor were composed of 30 wt % gas and 70 wt % liquid, whereas those from the thermal degradation of PP were composed of 10 wt % gas and 90 wt % other fractions (including a small liquid fraction and a lot of waxy solid). Analysis of gas chromatography (GC) showed that both gaseous fractions included C_3H_6, C_2H_6, C_2H_4, C_2H_2, CH_4, and hydrogen gas. Gas chromatography–mass spectrometry (GC–MS) was used to measure the liquid fractions in the degradation products of PP/PPMA = 80/10 and PP/PPMA/OMMT = 80/10/5 (by weight) mixtures during pyrolysis at 700 °C. The results showed that the degradation products of the PP/PPMA mixture included various alkenes with a carbon number varying from 7–43. The compounds with higher carbon numbers were found in the mixture of liquid fractions and waxy solids (Figure 5a). In contrast, the main liquid fractions in the degradation products of the PP/PPMA/OMMT mixture included alkenes with carbon number ranging from 5–9 (such as 2-pentene, 3-methyl-1-pentene, 3-methyl-3-hexene, 2-methyl-1-heptene, and 2,3-dimethyl-3-heptene) and aromatic hydrocarbons with 7–9 carbon atoms (toluene for C_7H_8, xylene for C_8H_{10} and mixture of ethyltoluene and trimethylbenzene for C_9H_{12}) (Figure 5b). The existence of a lot of aromatic hydrocarbons in the degradation products of PP/PPMA/OMMT further confirms the catalytic degradation of PP by a cationic mechanism due to the presence of OMMT.

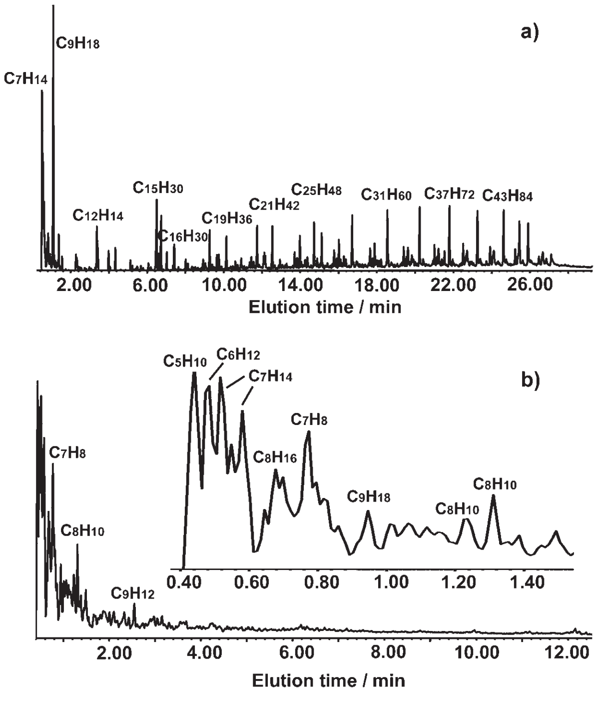


Figure 5. Gas chromatograms of the liquid fractions in the degradation products of a) PP/PPMA = 80/10 and b) PP/PPMA/OMMT = 80/10/5 (by weight).

Possibility of carbenium ions participating in the carbonization of the degradation products of polypropylene: Based on the above analysis, it is concluded that the effect of the combined catalysts on the yield of MWNTs might result from the formation of carbon sources that are easily transformed to MWNTs, such as hydrocarbons with 1–3 carbon atoms. Considering possible contact accompanied by interaction between OMMT and Ni_2O_3 in the PP matrix during the one-pot pyrolysis, a two-stage pyrolysis was designed. First, a PP/PPMA/OMMT mixture (for catalytic degradation) and a PP/PPMA mixture (for thermal degradation) were degraded at 700 °C, and then their degradation products were passed respectively through Ni_2O_3 at 700 °C. Although in this case it is impossible for the OMMT to come into contact with the Ni_2O_3, the yield of MWNTs in the case of catalytic degradation is still higher than that from thermal degradation (Table 1). This demonstrates that the degradation products of PP from catalytic degradation are more easily catalyzed in situ by Ni_2O_3 to form MWNTs. However, the yield of MWNTs in the case of catalytic degradation is lower in the two-stage pyrolysis than in the one-pot pyrolysis. It is possible that the contact between OMMT and Ni_2O_3 further promotes the yield of the MWNTs in the one-pot pyrolysis. To confirm this assumption, the following experiments were designed: case 1, only Ni_2O_3 was put into the pyrolyzer at 700 °C, then 10 mL of 1-hexene was added over one minute; case 2, Ni_2O_3 and H–ZSM-5 were separately put into the pyrolyzer at 700 °C, then 10 mL of 1-hexene was added within one minute; case 3, after Ni_2O_3 and H–ZSM-5 were first mixed together, the mixture was put into the pyrolyzer at 700 °C, then 10 mL of 1-hexene was added within one minute. The results showed the yield of MWNTs in this order: case 3 > case 2 > case 1 (Table 2). It is logical for the yield of MWNTs in case 1 to be the lowest. The higher yield of MWNTs in case 3 relative to case 2 probably results from the existence of carbenium ions during the carbonization of carbon sources, as this situation is impossible in case 2. Recently, Kazansky showed that neither the adsorbed carbeni-

Table 2. Effect of combined catalysts on the MWNT yield from different carbon sources in the pyrolyzer at 700 °C.

Carbon source	Yield of MWNTs [wt %]		
	case 1[a]	case 2[b]	case 3[c]
propylene[d]	29.0	29.6	28.4
1-hexene[e]	8.0	10.6	21.7
1-dodecene[f]	5.8	8.6	19.9

[a] 0.3 g of Ni_2O_3. [b] 0.3 g of Ni_2O_3 and 0.5 g of H–ZSM-5, separately. [c] Mixture of Ni_2O_3/H–ZSM-5 = 0.3 g/0.5 g. [d] Propylene was added at 600 mL min^{-1} for 2 min. [e] 10 mL of 1-hexene was added within 1 min. [f] 10 mL of 1-dodecene was added within 1 min.

um ions nor the adsorbed carbonium ions could be considered as free species because they are strongly electrostatically bonded to the surface of solid acids.[16]

We choose propylene as a typical component of the gaseous fraction and 1-dodecene as a typical component of the liquid fraction of the degradation products of PP to investigate effects of composition and combined states of the catalysts on the yield of MWNTs (Table 2). Interestingly, the same phenomena was displayed for both 1-hexene and 1-dodecene, but the yield of MWNTs obtained from propylene was almost the same for the three different catalyst mixtures. On this basis, it is believed that the existence of the carbenium ions promotes the yield of MWNTs from the carbon sources with higher carbon numbers only. This is probably the result of the ready occurrence of hydride transfer reactions in these carbon sources. Therefore, if contact between Ni_2O_3 and solid acid occurs in the PP mixture during pyrolysis, the active intermediate states are not free-radical condensates, but rather carbenium ions. The presence of carbenium ions can improve the formation of MWNTs for the following reasons; formation of more molecules with a lower carbon number, which can then easily be catalyzed by nickel to form MWNTs, and promotion of the conversion of molecules with a higher carbon number into MWNTs by hydride-transfer reaction.

Real active sites for carbonization of the degradation products of polypropylene: To completely understand the above combined catalysis, it is necessary to clarify whether Ni_2O_3 is a real active site for the formation of MWNTs. The presence of transition-metal particles as a catalyst is essential for the formation of CNTs in the pyrolysis process, and the diameter of the CNTs is determined by the size of the metal particles.[17] Normally the catalysts are prepared by reduction of supported metal oxides by hydrogen gas. Recently, some reports have demonstrated that metal oxides can be used directly as catalysts for the synthesis of CNTs.[18] The real active sites for formation of CNTs were in a metallic state. In situ reduction might occur through hydrogen gas from the decomposition of hydrocarbons and/or oxidation–reduction reactions between hydrocarbons and metal oxides. Therefore, a previous reduction seems to be unnecessary for synthesis of CNTs catalyzed by transition-metal oxides.

XRD was used to monitor the states of Ni_2O_3 before and after growth of MWNTs. In the XRD spectra of a PP/PPMA/OMMT/Ni_2O_3 = 80/10/5/5 (by weight) mixture (Figure 6, curve d), the diffraction peaks from OMMT are found at angles lower than 5°, inferring the intercalated structure of the above mixture. The diffraction peaks of PP, OMMT, and Ni_2O_3 in the charred residue disappeared completely after pyrolyzation at 700 °C (Figure 6, curve e). Meanwhile three new diffraction peaks appeared, one is ascribed to the charred materials with graphitic structure and the others to the metallic state of nickel (Ni) (Figure 6, curves e and a). Comparing XRD patterns of Ni with those of Ni_2O_3 (Figure 6, curves a and b), it was clear that nickel existed as Ni_2O_3 in the mixture of PP/PPMA/OMMT/Ni_2O_3 and as elemental Ni in the charred residue of the PP/PPMA/OMMT/Ni_2O_3 mixture. This showed that Ni_2O_3 was reduced to Ni during pyrolysis.

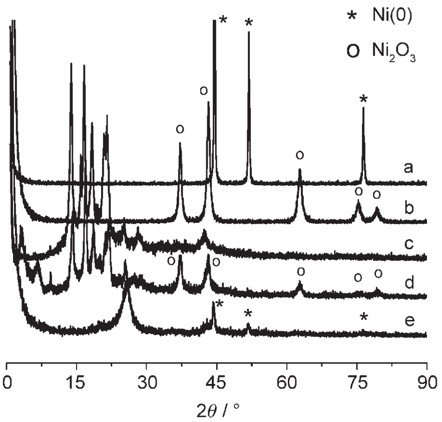


Figure 6. XRD profiles of a) Ni from reduction of Ni_2O_3 by H_2, b) Ni_2O_3, c) PP, d) PP/PPMA/OMMT/Ni_2O_3 = 80/10/5/5 (by weight), e) the charring products of (d).

There are two possible pathways to reduce Ni_2O_3 into Ni; one from hydrogen gas and the other from the degraded hydrocarbon products of PP. The degradation of PP can provide an amount of hydrogen gas and various hydrocarbon products, according to measurements by GC and GC–MS. There was no change in the diffraction peaks of Ni_2O_3 in the XRD profile after heating for 6 min in the pyrolyzer at 700 °C. However, after only a little propylene was passed through Ni_2O_3 (or a Ni_2O_3/PP mixture was heated) at 700 °C for 3 min in the pyrolyzer, the diffraction peaks of Ni_2O_3 in the XRD profiles became very weak and even disappeared, and those of Ni appeared (Figure 7, curves c and d). This means that the nickel had been changed from Ni_2O_3 into Ni in the initial period of MWNT growth. Some previous reports showed that the formation of carbon nanofibers (CNFs) on polycrystalline Ni started with formation of metastable Ni_3C, which later decomposed into Ni and C, ac-

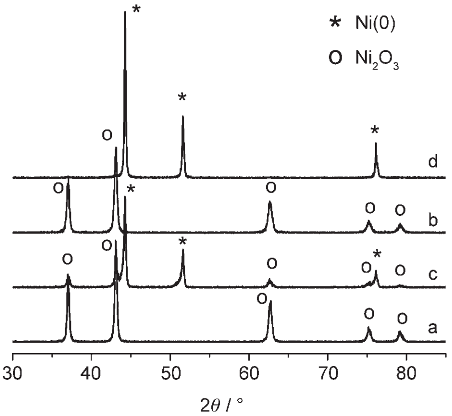
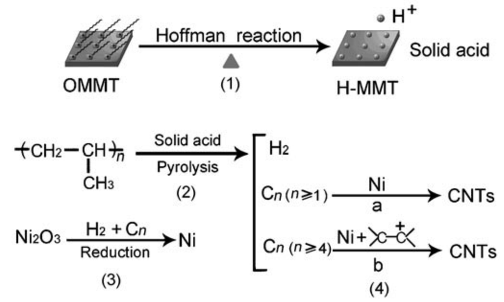


Figure 7. XRD profiles of a) Ni_2O_3 and its derivatives from the following treatments: b) heating for 6 min at 700 °C, c) after heating for 3 min at 700 °C, a little propylene gas passing through the Ni_2O_3, d) Ni_2O_3/PP mixture heated at 700 °C for 3 min.

cording to XRD measurements.[19] However, a similar phenomenon in the reduced Ni_2O_3 at 700 °C was not observed in our experiments, possibly indicating that the metastable Ni_3C could not form or had already decomposed at 700 °C.[19b] The Ni state was maintained after formation of MWNTs from PP (Figure 6, curve e). The above results demonstrate that the Ni_2O_3 was not the active catalytic species for the growth of MWNTs, and that the metallic Ni from the in situ reduction was the real active catalytic species, as had been previously reported.[18a,b]

Mechanism of combined catalysis for formation of MWNTs from polypropylene: The mechanistic aspect of the combined catalysis for the formation of MWNTs from polypropylene is depicted in Scheme 1. Brønsted acid sites are first created on the MMT layers to form H–MMT after the thermal decomposition of alkylammonium in the OMMT during pyrolysis (1). Then H–MMT acts as a strong catalyst for catalytic degradation of PP by a cationic mechanism (2). In general, the isomerization, cyclization, aromatization, and hydride transfer would take place during the catalytic degradation of PP, which leads to the formation of alkene, cycloalkanes, cycloalkenes, and aromatic hydrocarbons in the degradation products.[7a] The catalytic degradation of PP will afford gas and liquid fractions with lower carbon numbers than the fractions afforded by thermal degradation. In the third step (3), Ni_2O_3 is reduced to Ni in situ, probably by H_2 and/or other degradation products from the catalytic degradation of PP. The degradation products will be catalyzed to form CNTs by a dissociation-diffusion-precipitation process (4).[20] Here, the molecules with lower carbon numbers (a) in the degradation products of PP are easily catalyzed by Ni in situ to form MWNTs. In addition, the molecules with higher carbon numbers (b), in the degradation products of PP, will be easily catalyzed by Ni to form MWNTs due to the existence of carbenium ions in the reaction system. Carbenium ions can accelerate the dehydrogenization of hydrocarbons by Ni catalysts by a hydride transfer reaction. In contrast, molecules with higher carbon numbers, main products in thermal degradation of PP, were difficult to transform into the MWNTs. The above mechanism also applies to the combined catalysts of other solid acids, containing Brønsted acid sites, with Ni catalysts.



Scheme 1. Mechanism for the combined catalysis for the formation of MWNTs from polypropylene during pyrolysis.

Conclusion

The catalyst H–MMT used in the degradation of PP strongly influences the carbonization behavior of PP and the formation of MWNTs. That the combination of OMMT and the nickel catalyst leads to higher yields of MWNTs during pyrolysis is due to the Brønsted acid sites upon the H–MMT layers and the metallic Ni formed in situ from the reduction of Ni_2O_3 during the transformation of PP into MWNTs. The presence of carbenium ions as intermediates in the catalytic degradation of PP promotes the formation of MWNTs from the degradation products as carbon sources, especially those with higher carbon number. The above mechanism identified during pyrolysis of PP should be applicable to the carbonization process of recycled PP and should help in the understanding of the effect of combined catalysis on the fire retardancy of PP.[21] Research on combined catalysis for the synthesis of CNTs from other polymers and recycled polymers is in progress.

Experimental Section

Materials and preparation of samples: Polypropylene (PP, melt-flow index of 0.8 $g\,min^{-1}$) was mixed with Ni_2O_3 (from Lingfeng Chemical Company of Shanghai) and inorganic solids in a Brabender mixer at 100 rpm and 190 °C for 10 min. Inorganic solids include Na^+–montmorillonite (Na–MMT, with a cation exchange capacity value of 119 mequiv per 100 g from Kunimine Co.), organic-modified montmorillonite (OMMT, Closite 15 A from Southern Clay, organic modifier: dimethyl-dihydrogenated-tallow quaternary ammonium salt, modifier concentration: 125 mequiv per 100 g clay), $NH_4^+Cl^-$-modified montmorillonite (NH_4–MMT, prepared by complete ion-exchange in this Laboratory), commercial H-form ZSM-5 (H–ZSM-5), and NaOH modified H–ZSM-5 (Na–ZSM-5, prepared in this Laboratory). 10 wt % of maleated polypropylene (PPMA, acid value 26 mg KOH g^{-1}) was added into the above mixture as a compatibilizer. To observe char formation of PP during pyrolysis, a portion of the above PP mixture was put into a pyrolyzer and pyrolyzed at 700 °C. This process is called a one-pot pyrolysis. After the gaseous fraction was released, the charred residue was collected. The charred residue was purified with hydrofluoric acid (HF) and nitric acid (HNO_3) to eliminate MMT or ZSM-5, amorphous carbon, and most of the Ni. HF effectively dissolves inorganic solids. Based on reference [22], HNO_3 can effectively oxidize the amorphous carbon on the surface of CNTs and dissolve the Ni catalyst. The charred residue was first immersed in the HF for 24 h, then the residue was washed by deionized water three times. The residue was then suspended in a concentrated HNO_3 solution and refluxed at 120 °C for 5 h. Then, the solution was centrifuged, the supernatant liquid was decanted off and the black sediment is resuspended in deionized water. This rinse procedure is performed three times. The yield of the MWNTs (y) is calculated by the amount of the purified char (M) divided by the amount of PP and PPMA (M_{PP}) in the used sample, i.e., $y=(M/M_{PP})\times 100\,\%$. All of the samples were weighed by using an analytical balance.

Characterization: Acidity testing of the above MMT materials was performed by pyridine adsorption. In a sealed tube, the sample (about 15 mg) was exposed to pyridine vapor at 150 °C for 1 h. Subsequently, the sample was transferred out of the pyridine vapor and kept at 150 °C for 1 h to remove the physically adsorbed pyridine. The resulting product was pelletized with KBr and characterized by using a FTIR spectrometer (BRUKER Vertex 70 FTIR). OMMT and NH_4–MMT were firstly calcined to form H–MMT under a nitrogen atmosphere at 700 °C before the adsorption of pyridine.

The purity and phase structure of the nickel catalyst and the charred products were obtained by XRD using a Rigaku D/MAX-IIB powder X-ray diffractometer with $Cu_{K\alpha}$ radiation. The morphologies of the as-prepared products were examined by using field-emission scanning electron microscopy (FE SEM, XL303SEM) and TEM (JEM-2010, operated at 200 kV voltage). High-resolution transmission electron microscopy (HRTEM, Philips CM200, 200 kV) was used to further characterize the morphologies and microstructures of the purified product. Raman spectroscopy (T6400, excitation-beam wavelength: 514.5 nm) was used to characterize the vibrational properties of the obtained MWNTs. Thermogravimetric analysis (TGA) was carried out by means of a Perkin–Elmer TGA 7 thermal analyzer. The samples were heated in air to 300 °C at a heating rate of 20 °C min^{-1} and allowed to equilibrate for 1 min before being heated from 300 to 900 °C at 1 °C min^{-1}. Gas chromatography (GC, SHIMADZU GC-14C) and gas chromatography–mass spectrometry (GC–MS, AGILENT 5975 MSD) were used to measure the composition of the degradation products.

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[1] a) R. J. Rowatt, *CHEMTECH* **1993**, *23*, 56–60; b) Y. Uemichi, *Catalysis (Japan)* **1995**, *37*, 286–291.

[2] a) J. Aguado, J. L. Sotelo, D. P. Serrano, J. A. Calles, J. M. Escola, *Energy Fuels* **1997**, *11*, 1225–1231; b) D. P. Serrano, J. Aguado, J. L. Sotelo, R. Van Grieken, J. M. Escola, J. M. Menendez, *Stud. Surf. Sci. Catal.* **1998**, *117*, 437–444; c) D. P. Serrano, J. Aguado, J. M. Escola, *Ind. Eng. Chem. Res.* **2000**, *39*, 1177–1184; d) C. Breen, P. M. Last, *J. Mater. Chem.* **1999**, *9*, 813–818; e) C. Breen, P. M. Last, S. Taylor, P. Komadel, *Thermochim. Acta* **2000**, *363*, 93–104; f) C. Breen, S. Taylor, E. Burguin, M. Centeno, *J. Colloid Interface Sci.* **2002**, *247*, 246–250.

[3] S. Iijima, *Nature* **1991**, *354*, 56–58.

[4] a) J. Bernholc, C. Roland, B. I. Yakobson, *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 706–715; b) C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, M. S. Dresselhaus, *Science* **1999**, *286*, 1127–1129; c) J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, *Science* **2000**, *287*, 622–625; d) P. G. Collins, A. Zettl, H. Bando, A. Thess, R. E. Smalley, *Science* **1997**, *278*, 100–103.

[5] a) S. C. Lyu, B. C. Liu, S. H. Lee, C. Y. Park, H. K. Kang, C.-W. Yang, C. J. Lee, *J. Phys. Chem. B* **2004**, *108*, 2192–2194; b) H. Hou, Z. Jun, F. Weller, A. Greiner, *Chem. Mater.* **2003**, *15*, 3170–3175; c) P. J. F. Harris, *Carbon Nanotubes and Related Structure*, Cambridge University Press, Cambridge, **1999**.

[6] a) D. Sarangi, C. Godon, A. Granier, R. Moalic, A. Goullet, O. Chauvet, *Appl. Phys. A* **2001**, *73*, 765–768; b) N. I. Maksimova, O. P. Krivoruchko, G. Mestl, V. I. Zaikovskii, A. L. Chuvilin, A. N. Salanov, E. B. Burgina, *J. Mol. Catal. A* **2000**, *158*, 301–307; c) N. A. Kiselev, J. Sloan, D. N. Zakharov, E. F. Kukovitskii, J. L. Hutchison, J. Hammer, A. S. Kutosonov, *Carbon* **1998**, *36*, 1149–1157; d) E. F. Kukovitsky, S. G. L'vov, N. A. Sainov, V. A. hustov, L. A. Chernozatonskii, *Chem. Phys. Lett.* **2002**, *355*, 497–503; e) H. Nishino, R. Nishida, T. Matsui, N. Kawase, I. Mochida, *Carbon* **2003**, *41*, 2819–2823; f) S. Jou, C. K. Hsu, *Mater. Sci. Eng. B* **2004**, *106*, 275–281; g) Y.-H. Chung, S. Jou, *Mater. Chem. Phys.* **2005**, *92*, 256–259.

[7] a) C. Vasile, P. Onu, V. Barboiu, M. Sabliovschi, G. Moroi, *Acta Polym.* **1985**, *36*, 543–550; b) A. Marcilla, A. Gomez, J. A. Reyes-Labarta, A. Giner, F. Hernandez, *J. Anal. Appl. Pyrolysis* **2003**, *68–69*, 467–480.

[8] a) K. Hernadi, A. Fonseca, J. B. Nagy, A. Siska, I. Kiricsi, *Appl. Catal. A* **2000**, *199*, 245–255; b) K. Mizuno, K. Hata, T. Saito, S. Ohshima, M. Yumura, S. Iijima, *J. Phys. Chem. B* **2005**, *109*, 2632–2637.

[9] T. Tang, X. C. Chen, X. Y. Meng, H. Chen, Y. P. Ding, *Angew. Chem.* **2005**, *117*, 1541–1544; *Angew. Chem. Int. Ed.* **2005**, *44*, 1517–1520.

[10] P. T. A. Reilly, W. B. Whitten, *Carbon* **2006**, *44*, 1653–1660.

[11] a) D. K. Smith, D. C. Lee, B. A. Korgel, *Chem. Mater.* **2006**, *18*, 3356–3364; b) G. S. B. Mckee, K. S. Vecchio, *J. Phys. Chem. B* **2006**, *110*, 1179–1186.

[12] M. Zanetti, G. Camino, P. Reichert, R. Mulhaupt, *Macromol. Rapid Commun.* **2001**, *22*, 176–180.

[13] E. P. Parry, *J. Catal.* **1963**, *2*, 371–375.

[14] a) J. R. Kim, J. H. Yoon, D. W. Park, *Polym. Degrad. Stab.* **2002**, *76*, 61–67; b) J. G. A. Pacheco, E. C. Graciliano, A. O. S. Silva, M. J. B. Souza, A. S. Araujo, *Catal. Today* **2005**, *107–108*, 507–512.

[15] a) P. Magnoux, C. Canaff, F. Machado, M. Guisnet, *J. Catal.* **1992**, *134*, 286–298; b) K. Moljord, P. Magnoux, M. Guisnet, *Appl. Catal. A* **1995**, *122*, 21–32; c) B. W. Wojciechowski, *Ind. Eng. Chem. Res.* **1997**, *36*, 3323–3335; d) G. A. D. Nassionou, P. Magnoux, M. Guisnet, *Microporous Mesoporous Mater.* **1998**, *22*, 389–398.

[16] V. B. Kazansky, *Catal. Today* **1999**, *51*, 419–434.

[17] N. M. Rodriguez, *J. Mater. Res.* **1993**, *8*, 3233–3250.

[18] a) J. H. Huang, H. N. Lin, C. C. Chuang, H. W. Lai, J. H. Hsu, *Diamond Relat. Mater.* **2005**, *14*, 744–748; b) Y. Tian, Z. Hu, Y. Yang, X. Wang, X. Chen, H. Xu, Q. Wu, W. Ji, Y. Chen, *J. Am. Chem. Soc.* **2004**, *126*, 1180–1183; c) K. Hernadi, A. Fonseca, J. B. Nagy, D. Bernaerts, A. A. Lucas, *Carbon* **1996**, *34*, 1249–1257.

[19] a) N. A. Jarrah, J. G. van Ommen, L. Lefferts, *J. Catal.* **2006**, *239*, 460–469; b) M. Bououdina, D. Grant, G. Walker, *Carbon* **2005**, *43*, 1286–1292.

[20] S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov, J. B. Nagy, *Science* **1994**, *265*, 635–639.

[21] T. Tang, X. C. Chen, H. Chen, X. Y. Meng, Z. W. Jiang, W. G. Bi, *Chem. Mater.* **2005**, *17*, 2799–2802.

[22] a) M. Monthioux, B. W. Smith, B. Burteaux, A. Claye, J. E. Fischer, D. E. Luzzi, *Carbon* **2001**, *39*, 1251–1272; b) F. H. Ko, C. Y. Lee, C. J. Ko, T. C. Chu, *Carbon* **2005**, *43*, 727–733.

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