

Transferring Polypropylene into Carbon Nanotubes via Combustion of PP/Zeolites (H-ZSM-5 or H-Beta)/Ni₂O₃

Rongjun Song,^{1,2} Bin Li,^{1,2} Shu Zhao,^{1,2} Liping Li^{1,2}

¹Department of Chemistry, College of Science, Northeast Forestry University, Harbin 150040, China

²Heilongjiang Key Laboratory of Flame Retarded Polymeric Materials, Education Department of Heilongjiang Province, China

Received 29 February 2008; accepted 21 November 2008

DOI 10.1002/app.29754

Published online 6 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In a simple device, two kinds of zeolites were successfully used as synergistic additive to promote formation of the multi-walled carbon nanotubes (MWNTs) from polypropylene (PP) via combustion. More importantly, this kind of process may potentially act as a new approach for recycling plastic wastes, because it could effectively transfer polyolefin wastes into valuable carbon materials. Experimental results demonstrated that the higher quality of MWNTs can be obtained from the mixture (PP/H-Beta/Ni₂O₃) than that from the mixture (PP/

H-ZSM-5/Ni₂O₃). At the same time, the yield of MWNTs from PP/H-ZSM-5/Ni₂O₃ system is much lower than that from PP/H-Beta/Ni₂O₃ under the same condition. The reason for the different effects of both types of zeolites on the morphology and the yield of the MWNTs was analyzed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3423–3428, 2009

Key words: polypropylene; multi-walled carbon nanotubes; zeolite

INTRODUCTION

The total amount of the plastic wastes generated by our society is growing rapidly. Landfilling is undesirable because of the low biodegradability of the plastic wastes, which has created a serious environmental problem. Thus, the effective disposal of the wastes has been a tough research topic needed to be explored. On the other hand, the wastes are also a reservoir of resource, which seems to be more significant at the resource-shortage nowadays.¹ Among all the plastic wastes, the polyolefin accounts for a majority of the plastic wastes. To date, there has been a substantial amount of literatures discussing this topic, with methods mainly transferring the plastic waste of polyolefin into hydrocarbon products and fuels through catalytic cracking reaction by acid zeolites.^{2–5} However, the products are still the mixture of various components with different carbon number and different structure so far. Recently, in a material literature,^{6,7} a new approach was put forward to resolve this problem, which is to transfer the polyolefin wastes into the valuable carbon materials, i.e., carbon nanotubes (CNTs). CNT is the most important one-dimensional nanostructured material, which possesses many appealing properties including semiconducting or metallic electrical behavior, high mechanical

strength, and interesting chemical and surface properties.⁸ Potential applications include mechanical actuators,⁹ electronics,¹⁰ catalysis,¹¹ sensors,¹² high-strength composites,¹³ and adsorbents.¹⁴ Therefore, how to synthesize efficiently CNTs has always been under significant investigation by a number of R and D groups since its first observation using electron microscope by Iijima.¹⁵ Thus, if the polyolefin wastes could be transferred effectively into the valuable carbon materials, i.e., CNTs, which can provide bifunctional action, first it can act as an effective approach for recycling large amount of virtually nondegradable polyolefin and second it provides a new approach to synthesize high-valued CNTs.

Chung et al. reported the synthesis of multi-walled carbon nanotubes (MWNTs) from catalytic pyrolysis of polypropylene (PP) by iron nanoparticles; however, the yield was not provided.¹⁶ Our previous results showed that PP mixture with SiO₂-Al₂O₃ supported nickel catalyst (S-Ni(0)) and organically modified montmorillonite (OMMT) could be highly transformed into MWNTs via combustion reaction.^{6,7}

The reason for the high-yield formation of MWNTs from PP via flame reaction catalyzed by combined catalyst has been investigated in some of our previous articles. Results indicated that the formation of montmorillonite (MMT) containing hydrogen proton (H-MMT) on MMT layers after thermal decomposition of alkylammonium in the OMMT would change thermal degradation of PP into catalytic degradation of PP as H-MMT could act as the

Correspondence to: R. Song (dew741105@163.com).

degradation catalyst of PP during pyrolysis.¹⁷ Furthermore, in another article, it has demonstrated that the reason that the combination of OMMT and nickel catalyst leads to a higher yield of MWNTs during pyrolysis is the combined catalysis of the Brønsted acid sites (A donor of H⁺) on the H-MMT layers and Ni from *in situ* reduction of Ni₂O₃ for transformation of PP into MWNTs.¹⁸ The presence of carbenium ions as intermediates in catalytic degradation of PP is more profitable to form MWNTs from the degradation products as carbon sources.

In this work, a much cheaper combined catalyst (zeolite/Ni₂O₃) was investigated to transfer PP (a model polymer of plastic wasters) into MWNTs. Two kinds of zeolite, i.e., H-beta and H-ZSM-5 bearing the Brønsted acid sites and Lewis acid sites (a donor of vacant orbit for acceptance of isolated electron pair), chosen and combined, respectively, with Ni₂O₃, were applied to catalyze the carbonization reaction of the degradation products came from PP via combustion. At the same time, a comparison was made for different effects of the addition of both zeolites into PP mixture on the morphology and the yield of the MWNTs.

EXPERIMENTAL

Materials and preparation of samples

PP (melt flow index of 0.8 g/min) was mixed with Ni₂O₃ (from Lingfeng Chemical Company of Shanghai, China) and zeolite in a Brabender mixer at 100 rpm and 190°C for 10 min. Ni₂O₃ ($d < 50$ nm) was provided kindly by Lingfeng Chemical Company of Shanghai, China. Commercial H-ZSM-5 (Si/Al = 38, $d < 10$ μm) and H-Beta (Si/Al = 70, $d < 10$ μm) zeolite were purchased from the Catalyst Factory of Nankai University.

For synthesizing the as-prepared product, about 5 g mixture was placed in an open crucible and burned at 700°C until the flame disappeared, the charred residue was collected. Then, the charred residue was purified with hydrofluoric acid (HF) and nitric acid (HNO₃) to eliminate zeolite, amorphous carbon, and most of Ni(0). HF belongs to a kind of effective solvent to dissolve inorganic solids. According to previous report,^{19,20} nitric acid can effectively oxidize amorphous carbon attached on the surface of CNTs and dissolve Ni catalyst. The charred residue was first immersed in the HF for 24 h. Then the residue was washed three times with deionized water. After that, the residue was suspended in concentrated nitric acid solution and refluxed at 120°C during 5 h. Then, the solution was centrifuged, the supernatant liquid was decanted off, and the black sediment was resuspended in deionized water. This rinse procedure was performed three times. The yield of the MWNTs (y) is

calculated by amount of the purified char (M) divided by amount of PP in the used sample, i.e., $y = (M/M_{PP}) \times 100\%$. All of the samples were weighed by analytical balance.

Characterization

Acidity testing of the both zeolite was done by pyridine adsorption. In a sealed tube, about 15 mg of the samples was exposed to the 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 FTIR spectrometer (BRUKER Vertex 70 FTIR).

The morphologies of the as-prepared products were examined with field-emission scanning electron microscopy (FE-SEM, XL303SEM) and transmission electron microscopy (TEM, JEM-2010, operated at 200 kV voltage). High-resolution transmission electron microscopy (HRTEM, Philips CM200, 200 kV) was performed to further characterize the morphologies and microstructures of the purified product.

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 and allowed to equilibrate for 1 min before being heated from 300 to 700°C at 1°C/min.

RESULTS AND DISCUSSION

The morphologies and microstructures of MWNTs formed from polypropylene via combustion reaction catalyzed by H-Beta/Ni₂O₃ cocatalyst and catalyzed by H-ZSM-5/Ni₂O₃ cocatalyst were compared.

The morphologies and microstructures of the as-prepared products were examined with SEM. The SEM images in Figure 1(a,b) show a typical sample of carbon products from the mixture (PP/H-Beta/Ni₂O₃ : 90/5/5). It could be seen that the as-prepared product contained an abundance of hair-like fibers, and these hair-like fibers had almost uniform distribution of diameters. Beside these fibers, there was not any other morphology of carbonaceous species existed in the as-prepared products. From this point, the quality of product obtained from mixture (PP/H-Beta/Ni₂O₃ : 90/5/5) was much higher than that of CNTs produced by some previous methods from polymer.^{6,7,16} As a comparison, H-ZSM-5 zeolite was chosen to replace H-Beta in the above PP mixture. From the image shown in Figure 1(c,d), it was evident that the different morphologies of as-prepared products had obtained from PP/H-ZSM-5/Ni₂O₃. The as-prepared products also consisted of some hair-like fibers with different diameter. However, the outer diameters of most fibers were bigger than that of the fiber from PP/H-Beta/Ni₂O₃.

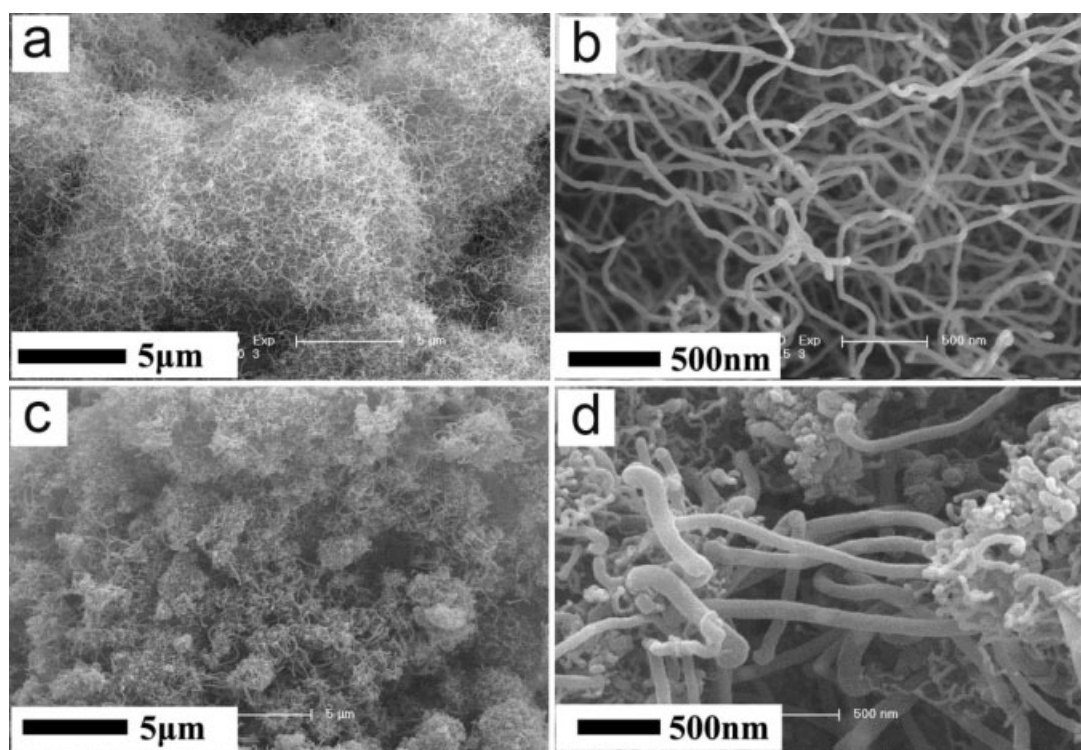


Figure 1 SEM image of the as-prepared products from mixture after combustion at 700°C. (a, b) SEM image (original magnification: 4864 \times and 38,911 \times) of the char from PP/H-Beta/Ni₂O₃ (90/5/5); (c, d) SEM image (original magnification: 4694 \times and 37,553 \times) the char from PP/H-ZSM-5/Ni₂O₃ (90/5/5).

Furthermore, lots of carbonaceous particles could be found in the as-prepared products.

Then, the TEM micrograph was used to characterize the microstructure of two kinds of carbon products from both of the PP mixture. TEM performed at intermediate magnification of the fiber-like product [Fig. 2(a)], confirmed that the hair-like fibers from PP/H-Beta/Ni₂O₃ was MWNTs with hollow centers. The detailed structure of a single tube of the purified MWNTs was given in an HRTEM image [Fig. 2(c)] and showed that lots of defects still appear in the alignment of the graphite layers, which result in distortion and disconnection of many coaxial tubes. However, the walls of pristine nanotube mainly consisted of graphite fringes which are well graphitized and a little amorphous carbon attaches on the outer surface of the tubules. Therefore, it can be demonstrated that the relative higher quality MWNTs could be synthesized from mixture (PP/H-Beta/Ni₂O₃ : 90/5/5) in contrast with some previous methods from polymer.^{6,7,16} Contrastively, the as-prepared product from PP/H-ZSM-5/Ni₂O₃ contained lots of amorphous carbon [Fig. 2(b)]. HRTEM image [Fig. 2(d)] shows the walls of pristine nanotube are not well graphitized, which are not concentric.

TGA was used to further evaluate the graphitized degree of the MWNTs from mixture (PP/H-Beta/

Ni₂O₃ : 90/5/5) (Fig. 3). The maximum weight loss occurred at 590°C. At the same time, the MWNTs decomposed a little when the temperature was below 500°C, which further demonstrates that the quality of product was much higher than that of CNTs provided by some previous methods from polymer.

Investigation of the relationship between the concentration of the H-Beta or H-ZSM-5 in mixture and the yield of the purified MWNTs

The effect of the content of H-Beta on the yield of MWNTs was investigated. The content of Ni₂O₃ was fixed 5% concentration in all composites. From Figure 4, it can be seen clearly that the yield of MWNTs produced from PP/H-Beta/Ni₂O₃ mixture increase dramatically with increase of the H-Beta concentration; however, when the concentration of H-Beta was increased further, the yield of MWNTs almost could not be change. The highest yielded value in these experiments was 52% obtained at 5 wt % H-Beta content. In Figure 4, the curve B indicates that same phenomenon appears for the PP/H-ZSM-5/Ni₂O₃ systems. Contrastively, the trend of both curves is same, whereas the yield of MWNTs from PP/H-ZSM-5/Ni₂O₃ system is much lower than that from PP/H-Beta/Ni₂O₃ under the same condition.

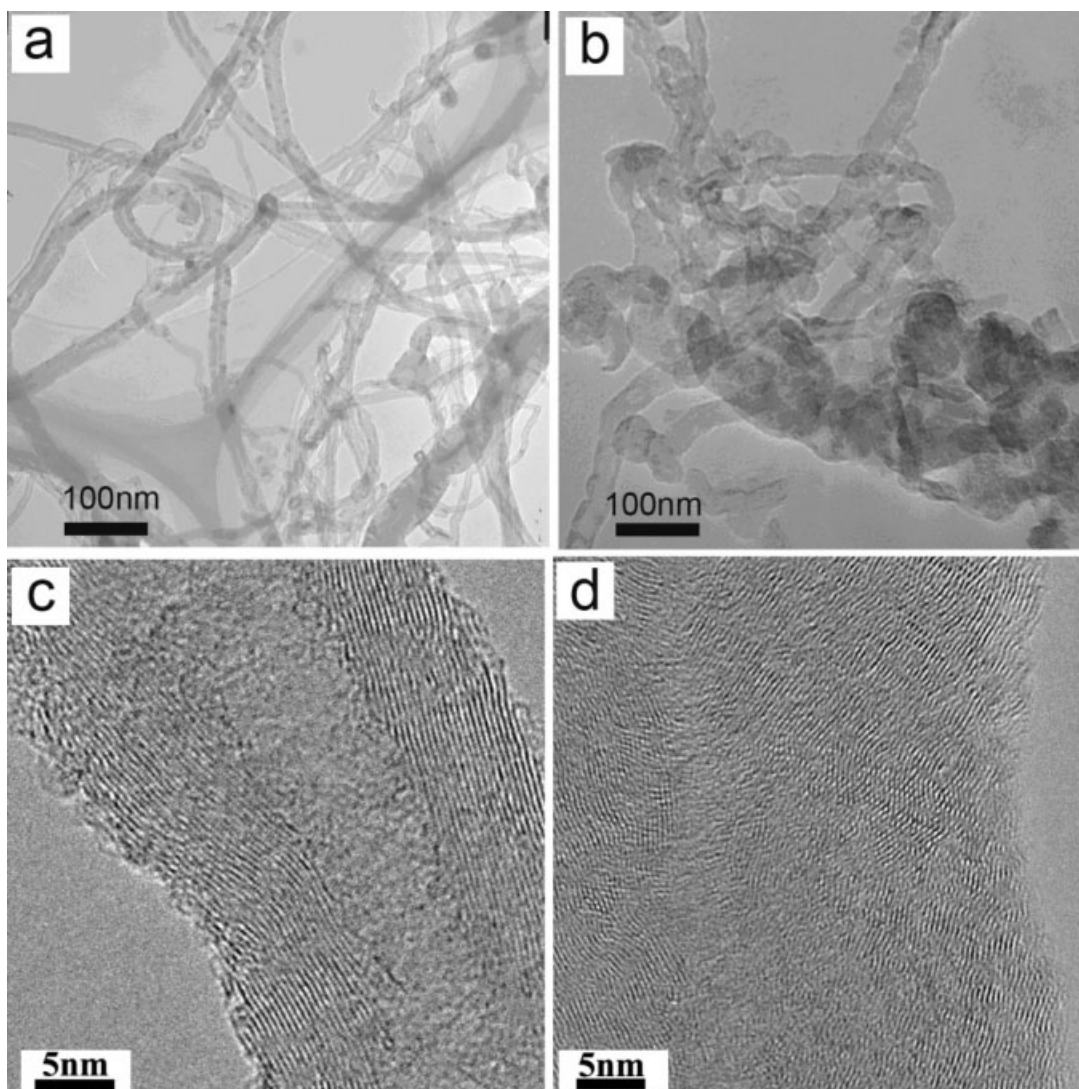


Figure 2 TEM photograph of the as-prepared products and purified MWNT from mixture after combustion at 700°C. (a, c) TEM image (original magnification: 100,000 \times and 450,000 \times) of the char from PP/H-Beta/Ni₂O₃ (90/5/5); (b, d) TEM image (original magnification: 100,000 \times and 400,000 \times) the char from PP/HZSM-5/Ni₂O₃(90/5/5).

Analysis of the reason for different action of two kinds of zeolites in the synthesis of MWNTs from PP/zeolite/Ni₂O₃ systems

According to our previous reports,^{17,18} the Brønsted acid and Lewis acid sites located on the surfaces of the zeolite should play an important role in promoting carbonization reaction of the degradation products catalyzed by Ni₂O₃. We wonder whether both kinds of zeolite with different acid characteristic will result in the different behavior in the synthesis of MWNTs from PP/zeolite/Ni₂O₃. As for H-Beta zeolite, it belongs to a kind of large pore and strong acidity molecular sieve, and H-ZSM-5, it is a kind of small pore and weak acidity molecular sieve, both of which belong to commercial product provide by Factory of Nankai University. The Brønsted and Lewis acidities of the zeolites were determined by pyridine

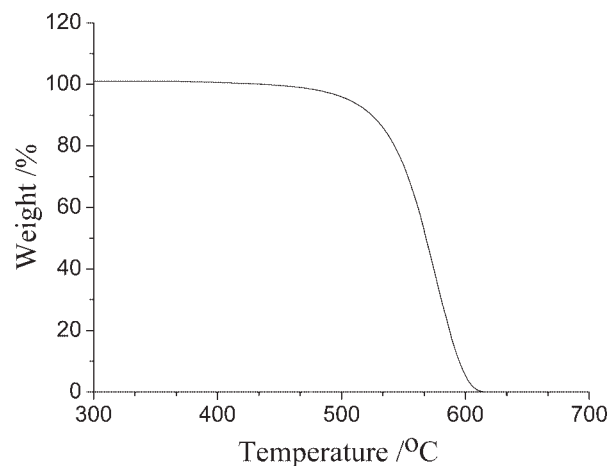


Figure 3 TGA weight loss curves of the MWCNTs from PP/H-Beta/Ni₂O₃ with 5 wt % of H-Beta and 3 wt % of Ni₂O₃.

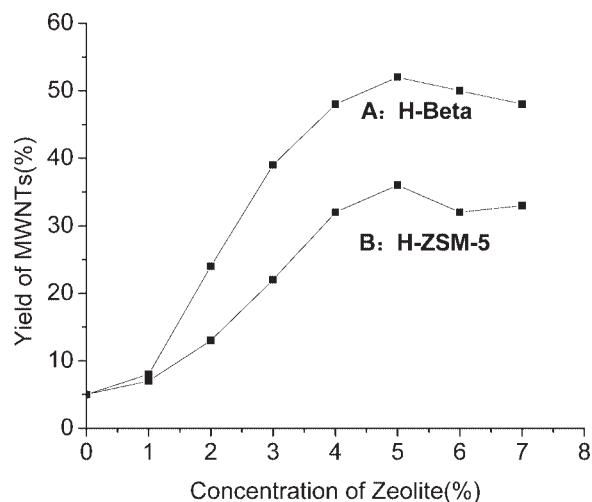


Figure 4 Effect of zeolite (H-Beta and HZSM-5) content in mixture on the yield of MWNTs.

adsorption using FT-IR spectroscopy. Figure 5 represents the IR spectra of pyridine adsorption on the H-ZSM-5 and H-Beta zeolite. On pyridine adsorption at 150°C, absorption bands associated with the chemisorbed pyridine were observed at 1549, 1491, and 1443 cm^{-1} . According to previous reports on IR studies in pyridine chemisorption,²¹⁻²³ the pyridine band at 1549 cm^{-1} can be assigned to pyridinium ions (C—C bands of pyridine adsorbed) which are characteristic of Brønsted acid sites, and the band at 1443 cm^{-1} to Lewis acid-coordinated pyridine (C—C bands of pyridine adsorbed). The band at 1491 cm^{-1} consisted of bands due to the Brønsted and Lewis acid sites. Because of the concentrations of both samples in KBr pellets is same (zeolite/KBr: 1/150, wt/wt), the intensity of characteristic absorption peaks in FTIR spectra can be made a comparison to indicate the acidity of zeolite relatively. It is evident that the acidity of H-Beta is stronger than that of H-ZSM-5 in this system, which is consistent with the results provided by fac-

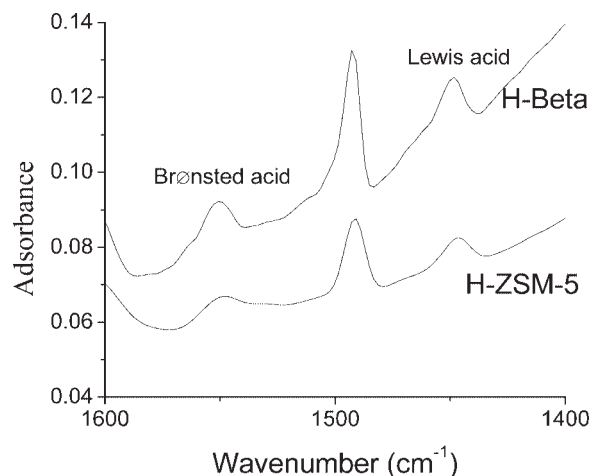


Figure 5 FTIR spectra of the adsorbed pyridine on H-Beta and HZSM-5 in the 1400–1600 cm^{-1} range after pyridine adsorption and then desorption at 150°C.

tory. It is well-known that the acid sites not only can result in the cracking reaction of bulky molecules (mainly by the acid sites on/near the external surface of zeolite) but also can induce the deposit of carbon species of small molecules (by the acid sites on the surface and in the pores of zeolite) under high temperature condition. Thus, as for both of PP/zeolite/ Ni_2O_3 mixture, much lower molecular hydrocarbon will be produced from PP under high temperature condition in the present of H-Beta zeolite. To date, as for CNT formation from hydrocarbons, it is widely accepted that the molecules with lower carbon number are more easily *in situ* catalyzed by Ni(0) to form MWNTs and relatively lower molecular hydrocarbon as carbon source is often in favor of perfect graphitization of CNTs. In terms of the relationship between MWNTs formation and acid sites, Tang and coworkers have demonstrated that it is profitable to promote MWNTs formation from the degradation products of PP via pyrolysis when Ni_2O_3 as catalyst.¹⁸

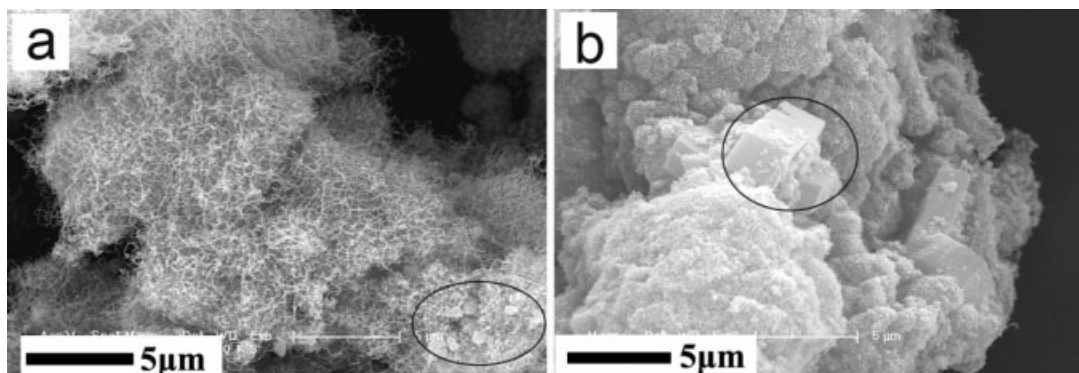


Figure 6 Morphology of zeolite in as-prepared product from mixture after combustion at 700 °C. (a) SEM image (Magnification: 4844×) of the char from PP/H-Beta/ Ni_2O_3 (90/5/5); (b) SEM image (Magnification: 4694×) of the char from PP/H-ZSM-5/ Ni_2O_3 (90/5/5).

Thus because of stronger acidity property of H-Beta than H-ZSM-5, it will be more profitable to produce MWNTs from PP when H-Beta as synergistic additive.

Different stability of both zeolite during MWNT synthesis should be considered as another important factor to influence the morphology, structure, and the yield of MWNTs from PP/zeolite/ Ni_2O_3 mixture. From Figure 6(b), it is clearly seen that perfect H-ZSM-5 crystalloid structure can be seen in the as-prepared product, which indicates that the H-ZSM-5 zeolite is too stable to be destroyed even in high temperature. On the contrary, the H-Beta zeolite is not stable in high temperature, which has cracked into fragments under high temperature as shown in Figure 6(a). Cracked into lots of small-scale fragments would make acid sites no matter on the surface or inside the pore of H-Beta effectively be exposed to the aliphatic groups come from PP and thus the cracking reactions of hydrocarbon and deposition reactions of carbon would take place more efficiently.

CONCLUSIONS

In summary, a new approach was developed to transfer the polyolefin wastes (PP as a model of polyolefin wastes) into the valuable carbon materials, i.e., (MWNTs). In comparison with the combined catalyst (PP/HZSM-5/ Ni_2O_3 : 90/5/5), the higher yield and the relative higher quality MWNTs with unique distribution of diameters are produced from PP with the combined catalyst (PP/H-Beta/ Ni_2O_3 : 90/5/5). The reason for it can be attributed to two characteristics of H-Beta zeolite. First, H-Beta belongs to a kind of large pore and strong acidity molecular sieve. Second, cracking into fragments under high temperature would be more suitable for H-Beta to exert acid sites so that facilitate the formation of MWNTs in our systems. Owing to not completely

demonstrate some detail steps how the effect of acid zeolite on the formation of MWNTs, further research is on the way in our laboratory. In addition, further work will be done to make use of true waste polyolefin as carbon source for synthesis of MWNTs.

References

1. Uemichi, Y. *Catalysis (Japan)* 1995, 37, 286.
2. Aguado, J.; Sotelo, J. L.; Serrano, D. P.; Calles, J. A.; Escola, J. M. *Energy Fuels* 1997, 11, 1225.
3. Serrano, D. P.; Aguado, J.; Sotelo, J. L.; Van Grieken, R.; Escola, J. M.; Menendez, J. M. *Stud Surf Sci Catal* 1998, 117, 437.
4. Serrano, D. P.; Aguado, J. J.; Escola, M. *Ind Eng Chem Res* 2000, 39, 1177.
5. Breen, C.; Last, P. M. *J Mater Chem* 1999, 9, 813.
6. Tang, T.; Chen, X. C.; Meng, X. Y.; Chen, H.; Ding, Y. P. *Angew Chem Int Ed Engl* 2005, 44, 1517.
7. Tang, T.; Chen, X. C.; Meng, X. Y.; Chen, H.; Ding, Y. P. *Angew Chem Int Ed Engl* 2005, 44, 1517.
8. Height, M. J.; Howard, J. B.; Tester, J. W.; Vander Sande, J. B. *J Phys Chem B* 2005, 109, 12337.
9. Landi, B. J.; Raffaele, R. P.; Heben, M. J.; Alleman, J. L.; Van Derveer, W.; Gennett, T. *Nano Lett* 2002, 2, 1329.
10. Avouris, Ph. *Chem Phys* 2002, 281, 429.
11. Li, W. Z.; Liang, C. H.; Qiu, J. S.; Zhou, W. J.; Han, H. N.; Wei, Z. B.; Sun, G. Q.; Xin, Q. *Carbon* 2002, 40, 787.
12. Wood, J. R.; Zhao, Q.; Frogley, M. D.; Meurs, E. R.; Prins, A. D.; Peijs, T.; Dustin, D.; Wagner, H. D. *Phys Rev B* 2000, 62, 7571.
13. Thostenson, E. T.; Ren, Z. F.; Chou, T. W. *Compos Sci Technol* 2001, 61, 1899.
14. Dillon, A. C.; Heben, M. J. *Appl Phys A* 2001, 72, 133.
15. Iijima, S. *Nature* 1991, 354, 56.
16. Chung, Y.-H.; Jou, S. *Mater Chem Phys* 2005, 92, 256.
17. Jiang, Z. W.; Song, R. J.; Bi, W. G.; Lu, J.; Tang, T. *Carbon* 2007, 45, 449.
18. Song, R. J.; Jiang, Z. W.; Bi, W. G.; Cheng, W. X.; Lu, J.; Huang, B. T.; Tang, T. *Chem Eur J* 2007, 13, 1534.
19. Monthieux, M.; Smith, B. W.; Burteaux, B.; Claye, A.; Fischer, J. E.; Luzzi, D. E. *Carbon* 2001, 39, 1251.
20. Ko, F. H.; Lee, C. Y.; Ko, C. J.; Chu, T. C. *Carbon* 2005, 43, 727.
21. Parry, E. P. *J Catal* 1963, 2, 371.
22. Poncelet, G.; Dubru, M. L. *J Catal* 1978, 52, 321.
23. Lee, J. S.; Boudart, M. *Catal Lett* 1993, 20, 97.