((Catch Phrase))

DOI: 10.1002/anie.200((will be filled in by the editorial staff))

Sustainable processing of waste plastics to produce high yield hydrogen-rich synthesis gas and high quality carbon nanotubes**

Chunfei Wu, Zichun Wang, Leizhi Wang, Paul T. Williams, Jun Huang**

It is estimated that about 8% of the world's oil production is used to manufacture plastic materials each year. The total production of plastics in the world increased from 1.5 million tonnes in 1950 to 230 million tonnes in 2009 (EU: 45 million tonnes in 2009).[1] From this burgeoning use of plastics arises a plastic waste stream which requires treatment. While there is recovery of energy from plastics via municipal waste to energy plants and increases in recycling (mainly mechanical recycling), there is a significant quantity of waste plastics which are disposed of by landfill. For example in the European Union 11.2 million tonnes of waste plastics were disposed by landfilling in 2009.[1] This huge amount of wasted potential hydrocarbon resource attracts much research interest as waste that could be used to provide resources for a more sustainable future.

Gasification, a thermal degradation process in the presence of a limited supply of oxygen, has been known for several decades for the production of gas from coal.[2] There has been recent interest in applying the technology for the gasification of wastes, including waste plastics for feedstock and energy recovery. Gasification of waste plastics produces a synthesis gas (syngas) including H_2, CH_4, CO and also CO_2. However, the commercialization of waste plastics gasification technology could be significantly improved if the gasification process could be developed to convert all of the carbon-compounds to valuable products rather than CO_2 and that the hydrogen yield could be enhanced to such an extent that a clean hydrogen fuel is produced. Catalysts are one of the key factors for maximizing the production of hydrogen from waste plastics gasification. However, deactivation of the catalyst by the deposition of coke as a carbonaceous reaction product has drawn extensive concerns,[3] particularly as the coke cannot be avoided during the process. Here, we introduce a creative method to turn the "negative" effect of carbon deposition into a "positive" way by manipulating the formation of carbon deposition on the catalyst in the form of carbon nano-tubes (CNTs). The unique properties of CNTs will undoubtedly have many applications in the areas of electronics,[4] biosensors,[5] energy storage and reinforced composites for aeroplanes etc.[6] Together with the production of clean H_2, the added value from CNTs will provide a step change to the process of gasification of waste plastics; thus makes the technology more economically feasible, environmentally friendly and resource sustainable.

In this research, the gasification of waste polypropylene using Ni/Cal-Al and Ni/Zn-Al catalysts under steam has been carried out in a two-stage reaction system (Figure S1, experimental method see the Supporting Information). After GC and GC/MS analysis, gas concentration and hydrogen production have been summarized in Figure 1. The H_2 concentration in the gas products reaches 64.3 Vol.% during gasification at 800 °C on the Ni/Ca-Al catalyst, which relates to 0.00082 Nm3 of H_2 generated from the gasification of 0.5 g of waste polypropylene. The maximum theoretical hydrogen production will be around 0.0024 Nm^3 if all the hydrogen in the plastics and the maximum reacted water was converted into hydrogen gas. Thus, about 34.1 Vol.% of potential hydrogen production (volume of the produced hydrogen divided by the maximum theoretical hydrogen production) was obtained in the presence of the Ni/Ca-Al catalyst.

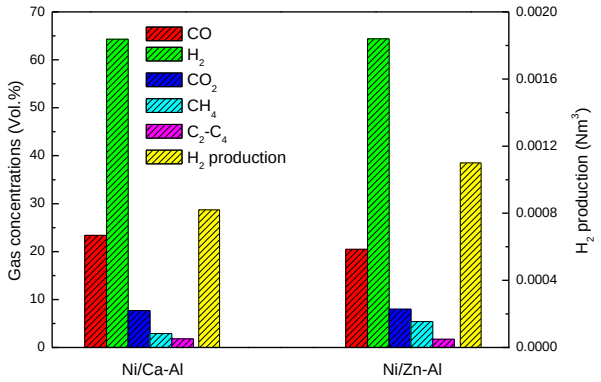


Figure 1. Gas concentration and hydrogen production for the gasification of polypropylene.

At the same time, carbon filaments were generated as coke by-product on the surface of the reacted catalyst, which have been detected by scanning electron microscopy (SEM) in Figure 2(a). Carbon filaments with uniform diameters and reasonable length could be clearly observed on the surface of the reacted Ni/Ca-Al catalyst. Transmission electron microscopy (TEM) images shown in Figure 2(b) were used to estimate that the carbon filament was about 50 nm in diameter and 10 μm in length. Graphene layers parallel to the axis of the carbon filament were observed from transmission electron microscopy (TEM) images (Figure 2(c)) indicating that tubular multi-walled carbon nano-tubes (MWCNTs)[7] was produced from the catalytic steam gasification of waste polypropylene. With graphene walls parallel to the filament axis, the highly crystallized CNTs should exhibit high electrical conductivity, thermal conductivity and mechanical strength.[8]

The comparison of our MWCNTs from waste polypropylene gasification and the commercial MWCNTs from Chengdu Organic Chemicals has been investigated by Raman spectroscopy and shown in Figure 3. The D band at around 1348 cm^{-1} is attributed to disordered amorphous carbon structures, while the G band at about 1571 cm^{-1} corresponds to tangential vibrations of the graphite carbons (i.e. crystallinity).[9] The second order Raman spectrum G' band at around 2683 cm^{-1} is due to the two-photon elastic scattering process.[10] The intensity of the D band normalized to the G band (I_D/I_G) is used to evaluate the degree of graphitization of CNTs. The I_D/I_G ratio of the CNTs from waste polypropylene gasification is

[*] Dr. C. Wu, Prof. P.T. Williams
Energy Research Institute
The University of Leeds
Leeds, LS2 9JT (United Kingdom)
E-mail: p.t.williams@leeds.ac.uk;
jun.huang@sydney.edu.au

Z. Wang, L. Wang, Dr. J. Huang
School of Chemical and Biomolecular Engineering
The University of Sydney
NSW 2006 (Australia)

[**] This work was supported by the UK Engineering and Physical Sciences Research Council under EPSRC Grant EP/D053110/1, the Worldwide Universities Networks (University of Leeds), International Exchange Scheme from the Royal Society (IE110273), and the Early Career Research Scheme from the University of Sydney.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

0.58, which is much lower than that of most reported CNTs (between 0.63 and 1.5)[11] and also the commercial MWCNTs (1.14) (Figure 3). It indicates that the highly graphitized CNTs were produced as by-products from polypropylene gasification. Furthermore, the higher intensity of the G' band (ratio of $I_{G'}/I_G$ is around 0.94) of the CNTs from gasification demonstrates that a higher purity of MWCNTs were produced from this research compared with the selected commercial MWCNTs ($I_{G'}/I_G$ ratio of 0.64 in Figure3). Since it is well know that normalization of the intensity of G' to the G band ($I_{G'}/I_G$) indicates the purity of CNTs, as the appearance of the G' band (two photons scattering) only happens on the ordered carbons.[9]

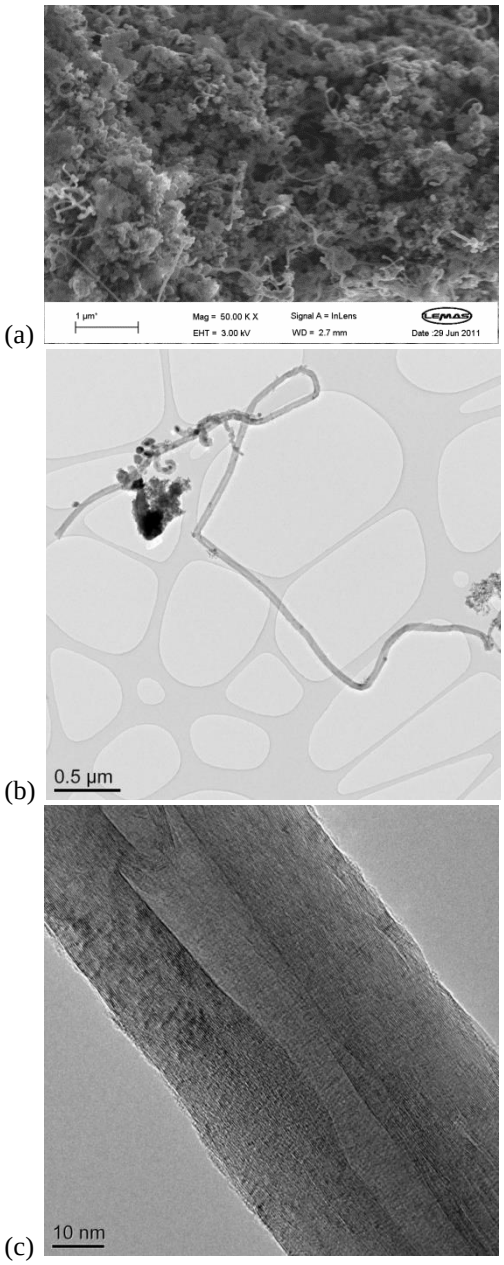


Figure 2. Morphology of the carbon nanotubes on the surface of the 20 wt.%Ni/Ca-Al (1:1) catalyst. (a) Scanning electron microscopy at a magnification of 50,000; CNTs were observed on the surface of the reacted catalyst; (b) and (c) transmission electron microscopy.

The mass of CNTs generated during gasification could be calculated by temperature programmed oxidation (TPO) of the coked catalyst. As shown in Figure 4, the differential thermogravimetry (DTG)-TPO results show two oxidation peaks at 520 and 682 °C for

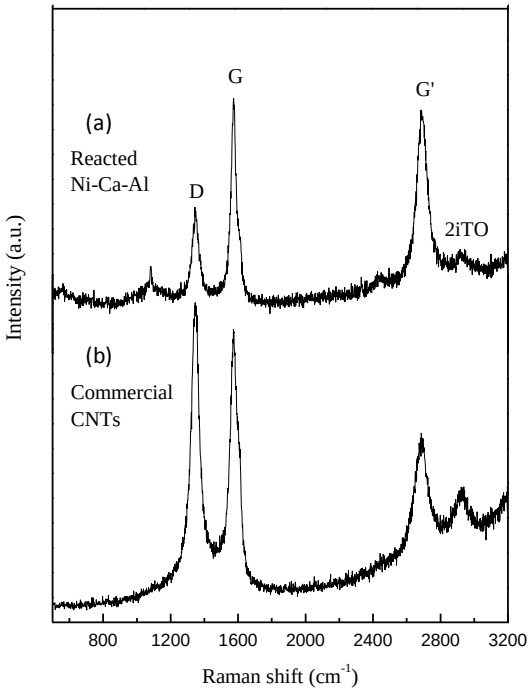


Figure 3. Raman spectroscopy of the carbon nanotubes on the reacted Ni/Ca-Al catalyst (a) and the commercial CNTs (b).

the reacted Ni/Ca-Al catalyst caused by the oxidation of the amorphous carbons and the CNTs, respectively.[12] After calculation, CNTs contributed 20 wt.% of the weight of the reacted Ni/Ca-Al samples, therefore around 0.053 g of CNTs was generated during the gasification of 0.5 g polypropylene.

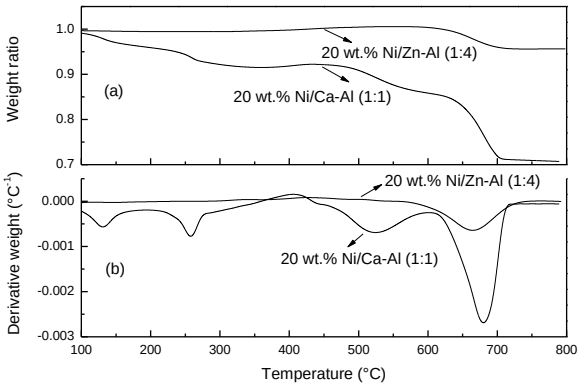


Figure 4. Temperature programmed oxidation of the reacted catalyst.

Moreover, the yield of H_2 and CNTs can be easily tuned by changing catalysts. The hydrogen production was enhanced from 0.00082 to 0.0011 Nm^3 with a corresponding reduction of the amount of CNTs from 0.053 to 0.012 g by changing the catalyst from Ni/Ca-Al to Ni/Zn-Al for the gasification of 0.5 g polypropylene. Interestingly, both types of catalysts showed similar gas concentrations as described in Figure 1. However, total gas yield (weight of gas divided by the weight of polypropylene) was 137.8 and 186.1 wt.% for the Ni/Ca-Al and the Ni/Zn-Al catalyst, respectively (Table S1). Therefore, utilizing Ni/Zn-Al catalyst to selectively promote catalytic interactions between steam and carbon-containing compounds can realize higher gas and hydrogen production with less CNTs generation during the gasification of

waste polypropylene, while the concentration of H_2 in the gas stream remains constant.

From the results shown here about it can be proposed that 1 tonne/day of CNTs (10 wt.% of the weight of the waste plastics) could be potentially generated together with H_2 production around 16800 Nm^3/day for a commercial gasification plant running with a capacity of 10 tonnes/day waste plastics. Carbon nanotubes are a very high value product with a wide range of applications. In addition, the waste plastics gasification plant using catalytic steam gasification has the potential to produce high yields of a syngas rich in hydrogen, providing an energy carrier to fuel the future. Our method also shows great flexibility for commercial application, the production of H_2 and CNTs can be adjusted by simply replacing catalysts. Without changing any other operation parameters, increasing the production of H_2 or CNTs can be easily realized according to the requirements of the chemical, hydrogen and materials end-markets.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

Keywords: carbon nanotubes · hydrogen · pyrolysis · polypropylene · nickel

[1] The Fact-Plastics Europe, **2010**.
[2] M. W. Haenel, *Angewandte Chemie International Edition in English* **1988**, *27*, 1385-1386.
[3] a)J. Li, R. Yan, B. Xiao, D. T. Liang, L. Du, *Environmental Science & Technology* **2008**, *42*, 6224-6229; b)M. Asadullah, S. I. Ito, K. Kunimori, M. Yamada, K. Tomishige, *Environmental Science & Technology* **2002**, *36*, 4476-4481.
[4] W. Liang, M. Bockrath, D. Bozovic, J. H. Hafner, M. Tinkham, H. Park, *Nature* **2001**, *411*, 665-669.
[5] W. Yang, K. R. Ratinac, S. P. Ringer, P. Thordarson, J. J. Gooding, F. Braet, *Angewandte Chemie International Edition* **2010**, *49*, 2114-2138.
[6] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, *Science* **2002**, *297*, 787-792.
[7] S. Lijima, *Nature* **1991**, *354*, 56-58.
[8] K. B. K. Teo, C. Singh, M. Chhowalla, W. I. Milne, in *Encyclopedia of nanoscience and nanotechnology* (Ed.: H. S. Nalwa), American Scientific Publishers, California, **2003**, pp. 665-686.
[9] R. A. DiLeo, B. J. Landi, R. P. Raffaelle, *Journal of Applied Physics* **2007**, *101*, 064307 064301-064305.
[10] R. Saito, A. Gruneis, G. G. Samsonidze, V. W. Brar, G. Dresselhaus, M. S. Dresselhaus, A. Jorio, L. G. Cancado, C. Fantini, M. A. Pimenta, A. G. Souza, *New Journal of Physics* **2003**, 157.151-157.115.
[11] a)M. G. Donato, S. Galvagno, G. Messina, C. Milone, A. Pistone, S. Santangelo, *Diamond and Related Materials* **2007**, *16*, 1095-1100; b)S. Cui, R. Canet, A. Derre, M. Couzi, P. Delhaes, *Carbon* **2003**, *41*, 797-809.
[12] a)C. Wu, P. T. Williams, *Applied Catalysis B-Environmental* **2010**, *96*, 198-207; b)J. H. Lehman, M. Terrones, E. Mansfield, K. E. Hurst, V. Meunier, *Carbon* **2011**, *49*, 2581-2602.

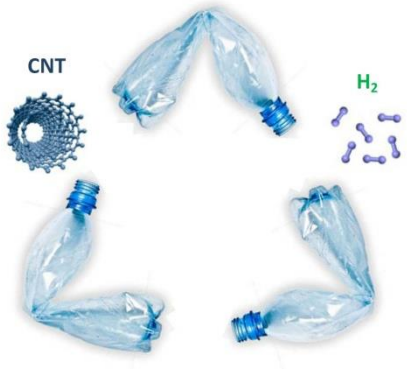
Entry for the Table of Contents

Layout 1:

((Catch Phrase))

Chunfei Wu, Zichun Wang, Leizhi Wang, Paul T. Williams*, Jun Huang*

Sustainable processing of waste plastics to produce high yield hydrogen-rich synthesis gas and high quality carbon nanotubes



The societal and industrial demand for plastics is ever increasing with a consequent increase in the production of plastic waste, most of which is disposed of to landfill representing a waste of a fossil fuel derived resource. Gasification provides a promising alternative to thermally recycle waste plastics to produce a synthesis gas which can be used as a fuel or as a chemical feedstock. The catalytic gasification process described here can process waste plastics to produce either a high yield, hydrogen-rich synthesis gas or high value, multi-walled carbon nano-tubes; a process that can be altered to produce the desired targeted end-product. Thereby, a waste material can be treated to produce hydrogen to fuel the future or carbon nano-tubes to meet the increasing demand for these valuable materials.