



The use of different metal catalysts for the simultaneous production of carbon nanotubes and hydrogen from pyrolysis of plastic feedstocks



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ABSTRACT

Nickel, iron, cobalt and copper catalysts were prepared by impregnation and used to produce carbon nanotubes and hydrogen gas from a LDPE feedstock. A two stage catalytic pyrolysis process was used to enable large yields of both products. Plastics samples were pyrolysed in nitrogen at 600 °C, before the evolved gases were passed to a second stage and allowed to deposit carbon onto the catalyst at a temperature of 800 °C. Carbon nanotubes were successfully generated on nickel, iron and cobalt but were barely observed on the copper catalyst. Iron and nickel catalysts gave the largest yield of both hydrogen and carbon nanotubes as a result of metal-support interactions which were neither too strong, like cobalts, nor too weak like copper. These metal support interactions proved a key factor in CNT production. A nickel catalyst with a weaker interaction was prepared using a lower calcination temperature. Yields of both carbon nanotubes and hydrogen gas were lower on the Ni-catalyst prepared at the lower calcination temperature, as a result of sintering of the nickel particles. In addition, the catalyst prepared at a lower calcination temperature produced metal particles which were too large for CNT growth, producing amorphous carbons which deactivate the catalyst instead. Overall the iron catalyst gave the largest yield of CNTs, which is attributed to both its good metal-support interactions and iron's large carbon solubility.

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1. Introduction

Thermal treatments such as pyrolysis are well-known methods for producing valuable gases and liquids from hydrocarbon feedstocks [1–3]. Among the gases produced, hydrogen is of particular interest as it is considered an important future fuel, since its combustion gives off only water. Whilst hydrogen is predominantly produced from reforming of natural gas, thermal treatment of hydrocarbon feedstocks such as waste plastics offer a more environmentally sound solution. Waste plastics are notoriously difficult to recycle, and thermal treatments such as pyrolysis can therefore offer an alternative waste management option to unsustainable landfill practices. Production of hydrogen from waste plastics is therefore a well-researched area, with a number of studies using pyrolysis and gasification techniques [4–9].

Transition metal e.g., nickel based catalysts are typically used for hydrogen production as they offer a higher catalytic activity than other transition metals, but are cheaper than other effective metal catalysts such as the noble metals [10]. However a major problem

associated with using transition metal based catalysts in thermal treatment of hydrocarbons is deactivation by coking [11], where carbon deposition builds on the catalyst surface. In an investigation into carbon deposition onto nickel catalysts Rostrup-Nielsen found three distinct types [12]. These were whisker type carbons, such as filamentous carbons, and pyrolytic and encapsulating carbons which deactivate the catalyst. As such a number of studies have aimed to reduce the build-up of carbon deposition on catalysts, in order to keep catalyst activities high [13–16].

However, recently it has been shown that some of the carbon deposits produced during plastics pyrolysis are valuable carbon nanotubes, with Kukovitsky et al. demonstrating production of crooked carbon nanotubes and filamentous carbons from pyrolysis of LDPE at 450 °C [17]. Carbon nanotubes are a valuable form of carbon with an increasingly large number of publications on the subject due to their potential for current and future uses in a wide range of industries including composites, microelectronics and energy applications [18,19]. Current mass production of CNTs comes from chemical vapor deposition of hydrocarbon gases such as methane and acetylene, however the pull of a low cost alternative which tackles waste management problems has encouraged research into production from plastic sources. As a result, a number of studies have started to tailor their pyrolysis processes toward carbon nan-

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otube production, achieving large yields with temperatures up to 900 °C [17,20–27]. Using a two stage process also enables large yields of hydrogen gas and carbon nanotubes can be produced simultaneously from a plastic source [20,26,28]. In previous studies by this research group a two stage process was devised where evolved pyrolysis gases were passed directly into the second catalysis stage [20,28]. A nickel catalyst was used, and large amounts of carbon nanotubes were produced in addition to large yields of hydrogen.

Catalysts play a key role in the production of carbon nanotubes and hydrogen. Whilst nickel catalysts excel at hydrogen production and are known to produce CNTs, other transition metals have also been researched for their potential for CNT production via CVD. Along with nickel, the most commonly used catalyst metals are iron [29–35], cobalt [36–38] and copper [39]. When catalyst metals have been directly compared it has been found that whilst all the metals are able to produce CNTs, iron catalysts give a large yield [31,33,35,40]. Liu et al. [40] investigated the effect of using iron, cobalt and nickel catalysts on CNT production from CVD of methane. The superior performance of the iron catalyst was attributed to iron's higher carbon solubility, which helps to promote the production of carbon nanotubes. In terms of hydrogen production however, iron and copper catalysts have shown much lower hydrogen yields than nickel and cobalt during steam reforming [10,41]. However, hydrogen is also produced during carbon deposition. When investigating the decomposition of methane into carbon nanotubes and hydrogen, Ago et al. found that decomposition was higher in iron catalysts than cobalt and nickel [29], producing higher hydrogen yields as a result.

In addition to the influence of metal types on CNT and hydrogen productions, the calcination temperature used during catalyst preparation is also an important factor [36,42–44]. For example, Chai et al. investigated the effect of the calcination temperature of a cobalt catalyst on CNT production using methane in a CVD process [36]. At low calcination temperatures, the interaction between the catalyst metal and support was weak, and during CNT production the catalyst underwent sintering, leading to metal particles too large for CNT production. As the calcination temperature was increased, however, the metal support interaction became stronger and as a result, the carbon nanotube yield increased. This was only true up to a certain point however, as the catalyst can become hindered by too strong a metal support interaction [45]. The calcination temperature likewise has an effect on hydrogen production [46–48]. Garcia et al. [48] investigated the effect of calcination temperature on hydrogen production and found that whilst lower calcination temperatures gave higher yields in the short term, the increased stability achieved with a higher calcination temperature led to a better overall performance in terms of long-term hydrogen production.

Currently, to our best knowledge, little information could be found on the investigation of different metal active sites and calcination temperatures on the simultaneous production of CNTs and hydrogen from pyrolysis of plastics. In this paper, a two stage catalytic pyrolysis process was used to produce carbon nanotubes and hydrogen simultaneously. The effect of catalysts prepared using different metals and calcination temperatures was investigated to determine the optimum catalyst for the process. Nickel, iron, cobalt and copper catalysts were investigated.

2. Experimental

2.1. Materials and reaction system

A low density polyethylene (LDPE) sample was obtained from ACROS Organics UK. Nickel, iron, cobalt and copper catalysts were

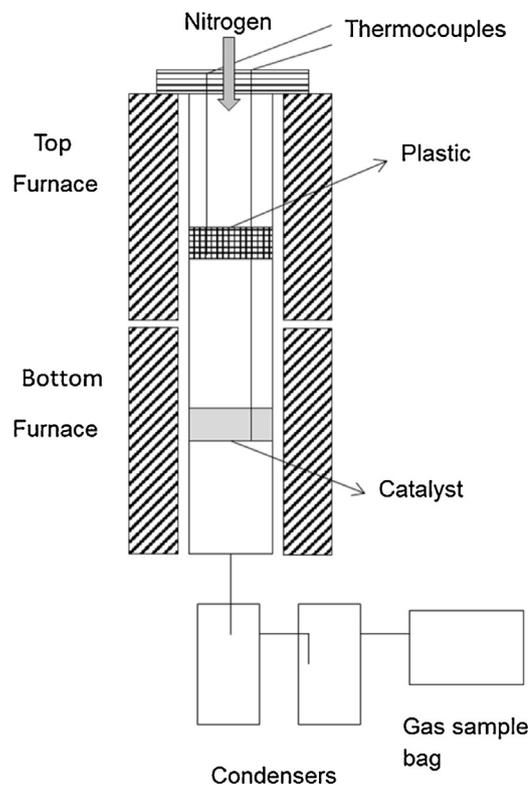


Fig. 1. Schematic diagram of the experimental setup.

prepared by an impregnating the metal onto an alumina support, so that a 10 wt% metal catalyst was produced. Metal nitrates and gamma Al_2O_3 were used as the raw materials. The metal nitrate was dissolved in ethanol, following which the alumina was added and the mixture left until it formed a slurry. This was then dried overnight in an oven at 50 °C to remove the remaining ethanol before calcination was undertaken. Two different calcination temperatures of 500 and 750 °C were used for the nickel catalyst to investigate the effect on CNT and H_2 production. The catalysts were heated to the desired temperature at a heating rate of 2 °C/min in an air atmosphere with a hold time of 3 h. Iron, cobalt and copper catalysts were also prepared using the same methodology, using a 750 °C calcination temperature. The catalysts were then crushed and sieved to give granules of between 0.05 and 0.18 mm.

The experimental system consisted of a two-stage pyrolysis reactor as shown in Fig. 1. The reactor was made of stainless steel and had a total length of 320 mm and an internal diameter of 22 mm, the top and bottom reactors were heated by separate furnaces. In each experiment 1 g of the LDPE was placed inside a sample boat and pyrolysed in first reactor, where the temperature was heated to 600 °C. The generated gaseous products were then passed through to the second reactor, held at 800 °C, and passed over 0.5 g of catalyst, allowing hydrogen to be produced with carbon deposition on the catalyst. Nitrogen was used as the carrier gas with a flow rate of 80 ml min⁻¹. The procedure was to heat the second gasification reactor to the desired temperature, then heat the first reactor to 600 °C at a heating rate of 50 °C min⁻¹ for a total reaction time of 30 min. The volatile products after the gasification process were passed through two condensers, where any condensed products were collected. The non-condensed gases were collected in a 25 l Tedlar™ gas sample bag. The reproducibility of the reaction system was tested and experiments were repeated to ensure the reliability of research results.

The gases collected in the gas sample bag were analysed by packed column gas chromatography (GC). Hydrocarbons (C1–C4)

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