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Research paper

Co-production of hydrogen and carbon nanotubes from real-world waste plastics: Influence of catalyst composition and operational parameters

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ABSTRACT

The use of Ni-Fe catalysts for the catalytic pyrolysis of real-world waste plastics to produce hydrogen and high value carbon nanotubes (CNT), and the influence of catalyst composition and support materials has been investigated. Experiments were conducted in a two stage fixed bed reactor, where plastics were pyrolysed in the first stage followed by reaction of the evolved volatiles over the catalyst in the second stage. Different catalyst temperatures (700, 800, 900 °C) and steam to plastic ratios (0, 0.3, 1, 2.6) were explored to optimize the product hydrogen and the yield of carbon nanotubes deposited on the catalyst. The results showed that the growth of carbon nanotubes and hydrogen were highly dependent on the catalyst type and the operational parameters. Fe/γ-Al_2O_3 produced the highest hydrogen yield (22.9 mmol $H_2/g_{plastic}$) and carbon nanotubes yield (195 mg $g^{-1}_{plastic}$) among the monometallic catalysts, followed by Fe/α-Al_2O_3, Ni/γ-Al_2O_3 and Ni/α-Al_2O_3. The bimetallic Ni-Fe catalyst showed higher catalytic activity in relation to H_2 yield than the monometallic Ni or Fe catalysts because of the optimum interaction between metal and support. Further investigation of the influence of steam input and catalyst temperature on product yields found that the optimum simultaneous production of CNTs (287 mg $g^{-1}_{plastic}$) and hydrogen production (31.8 mmol $H_2/g_{plastic}$) were obtained at 800 °C in the absence of steam and in the presence of the bimetallic Ni-Fe/γ-Al_2O_3 catalyst.

1. Introduction

The worldwide demand for plastics grows rapidly and inevitably produces large quantities of waste plastics. Over 60% of post-consumer plastics ends up in waste landfills or is incinerated, representing a waste of resource [1]. Thermal recycling via pyrolysis and gasification of waste plastics, into fuels and chemical products has been identified as a promising technology for tackling waste issues related to plastics [2,3]. In recent years, an attractive method of producing high value nanomaterials such as carbon nanotubes (CNTs) from waste plastics has been reported [4,5]. The produced CNTs were further utilised to produce reinforced materials which exhibited improved strength characteristics, implying the potential of the process in industrial applications [6].

Due to their extraordinary properties including chemical stability, electric conductivity, high surface area, etc., carbon nanotubes have been attracting worldwide attention [7–9]. Compared with other synthesis technologies which include arc discharge and laser ablation, chemical vapour deposition (CVD) is the most prevalent and versatile technology in terms of cost and bulk production. Research into CVD for CNT production has been reported to convert methane, ethylene, ethanol to carbon nanotubes through CVD [10,11]. Thermal conversion of plastics to carbon nanotubes can be achieved in two stage reactors, where solid plastics are pyrolysed to produce volatile materials in a first stage (temperature around 500 °C), followed by CVD at high temperature over a catalyst [12,13]. Hydrogen, which will be an important clean fuel in the future, can also be generated during this process.

The hydrogen yield and morphology of the product carbon nanomaterials can be varied with different operational parameters. The growth temperature is a key factor for carbon nanotubes production, as it effects both the hydrocarbon cracking and carbon diffusion rate. A novel fluidized bed reactor was investigated with different temperatures at different stages to obtain a balance between carbon production and diffusion on the catalyst, so that a continuous growth of carbon nanotubes was achieved [14]. Shen et al. [15] used a step-wise heating process for hydrogen and carbon materials production from methane. They reported that bamboo-shaped, multi-branched and onion-like carbons were deposited on the catalyst and their yield varied with increased catalyst temperature. In addition, an increase in catalyst temperature was shown to result in a higher yield of hydrogen from waste plastics [16]. In order to increase the hydrogen yield, steam has often

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been introduced to promote hydrocarbon reforming reactions which yields more gaseous product. However, as a consequence of steam addition, carbon deposited on the catalyst may also be gasified which leads to a lower carbon yield [17,18]. However, Zhang et al. [19] found that a low level injection of steam could improve the purity of carbon nanotubes without consuming excessive amounts of the carbon.

In addition to the operational parameters, other factors such as feedstock type, external energy (e.g. plasma enhanced) and catalyst to feedstock ratio have also been investigated to optimize the process [20–22]. However, the catalyst composition is considered to be the most influential factor for carbon nanotubes production. It is known that Ni-based catalysts are favorable for thermal conversion of hydrocarbons due to their effective catalytic activity and lower cost. Yang et al. [13] synthesized CNTs with an external diameter of 20–30 nm from polypropylene and polyethylene in a pilot-scale system using a H-Ni/Al_2O_3 catalyst. Wen et al. [23] used a Ni catalyst to form CNTs from polyolefin wastes, which showed good electrochemical performance as electrode material for supercapacitors. Whilst Ni based catalysts are commonly used for hydrogen production, Fe catalysts are more often utilised for carbon nanomaterial production. Acomb et al. [24] investigated the influence of different metal catalysts for the catalytic pyrolysis of low density polyethylene. They reported that an Fe/Al_2O_3 catalyst gave a higher conversion of the hydrogen in the plastic to H_2 gas (26.8% conversion), but also the Fe/Al_2O_3 catalyst produced a high carbon yield on the catalyst (26 wt.%) compared with Ni, Co and Cu based catalysts, due to the high carbon solubility of Fe.

Recently, bimetallic or trimetallic catalysts have received attention to further improve catalyst activity. A porous Ni-Cu-Co alloy catalyst was studied by Lua and Wang [25] for the decomposition of methane for hydrogen and carbon nanotubes production. The interaction between Cu and Fe was found to enhance the nucleation of nanotubes over Fe as well as minimize the bulk accumulation of carbon substrates [26]. In terms of hydrogen production, Wu and Williams [27,28] have suggested that a bimetallic Ni-Mg catalyst presented higher catalytic activity towards hydrogen production than a monometallic Ni catalyst. This was attributed to the reduced amount of monoatomic carbons produced and the enhanced physical stability of the catalyst with the bimetallic catalyst. The advantages of such multi-metal catalysts arises from good stability, smaller metal particle size and appropriate interaction between different metals [29]. Ni-Fe bimetallic catalysts have shown favorable performance for some studies, for example, Ni-Fe based on bio-char has been used in biomass gasification to increase tar conversion in an effective and economical way [30]. Enhanced methane dehydrogenation and longer catalyst life-time activity were found by Shen et al. [31] when using Ni-Fe/Mg(Al)O for CNTs production from methane. However, there are limited reports about using Ni-Fe bimetallic catalysts for the co-production of CNTs and H_2 from waste plastics.

The catalyst substrate is also an important factor for the synthesis of carbon nanotubes. Pure nickel particles without a substrate were found to be a difficult surface to deposit any carbons because of metal agglomeration [32]. The substrate acts not only as a support medium but also a reactant to catalyst and carbon precursors. The physical or chemical interaction between catalyst particles and support can stabilize the metal particles with a finely dispersed particle distribution [10]. As a number of reports in the literature have noted, the diameter of synthesized carbon nanomaterials were closely related to the catalyst metal particle size [33,34]. Thereby, the possibility of controlling the diameter of carbon nanotubes could be achieved. The effect of different catalyst support material properties on carbon nanomaterials production from methane was investigated by Takenaka et al. [35], and showed that Al_2O_3 and MgO supported Co catalysts gave higher carbon yields than Co/TiO_2 and Co/SiO_2. Ermakova et al. [36] reported that the morphology and structure of filamentous carbons on iron catalysts were strongly dependent on the chemical nature of the support.

Although there are a number of studies that have described the use of Fe or Ni based catalysts to catalyse the pyrolysis of hydrocarbons for carbon nanotubes production, most of them focus on small-molecule sized feedstock or single pure polymers. Available studies on Ni-Fe catalysts for the pyrolysis of real world waste plastics are quite limited. Moreover, the hydrogen yield and properties of carbon deposits using Ni-Fe with different supports, catalyst temperature and steam injection have not been systematically investigated. Therefore, this paper aims to explore monometallic Ni, Fe and bimetallic Ni-Fe catalysts for the pyrolysis of waste plastics. The effect of catalyst composition and substrate type on the yield and morphology of deposited carbon, as well as the hydrogen yield have been investigated. In addition, catalytic reforming of waste plastics under different catalyst temperatures and steam to plastic ratios were conducted to further optimize the process.

2. Materials and methods

2.1. Materials

Real-world waste plastics, including disposable drink cups, lunch boxes and plastic wraps, which are widely used for food packing, were collected and used for the process feedstock and were obtained from Mingjin Plastic Ltd, China. The plastic waste was crushed and ground using a liquid nitrogen grinder with screen meshsize between 0.1 and 1 mm. The mixed plastic waste composition was comprised of 40 wt.% sample bottles (mainly HDPE), 35 wt.% plastic bags (mainly LDPE), 20 wt.% preservative boxes (mainly PP) and 5 wt.% lunch boxes (mainly PS). The ultimate analysis of the material was 84.51 wt.% carbon, 13.85 wt.% hydrogen, 1.51 wt.% oxygen and 0.13 wt.% sulphur. Ash content of the mixed plastics was less than 1 wt.%.

Monometallic Ni or Fe based catalyst and bimetallic Ni-Fe catalyst were prepared using an impregnation method. Metal nitrates and two different crystalline forms of alumina (α-Al_2O_3 and γ-Al_2O_3, supplied by Sigma Aldrich, UK) were used as the support material. Both alumina forms are resistant to high temperature and are considered to be stable catalyst supports. Ni/α-Al_2O_3 was prepared starting with 5.503 g of Ni$(NO_3)_3{\cdot}6H_2O$ dissolved in ethanol, followed by addition of 10 g α-Al_2O_3, so that the initial metal loading was 10 wt.%. The precursors were stirred for 4 h using a magnetic stirrer and dried at 50 °C overnight to remove the remaining ethanol. The solid was then calcined at 800 °C with a heating rate of 10 °C min^{-1} and a hold time at 800 °C of 3 h under an air atmosphere. The other catalysts Ni/γ-Al_2O_3, Fe/α-Al_2O_3, Fe/γ-Al_2O_3 and Ni-Fe/γ-Al_2O_3 were synthesized using the same procedure. Bimetallic Ni-Fe catalyst was prepared with the same 10 wt.% of total metal loading but with a Ni to Fe molar ratio of 1–3, which was the optimum composition for the highest yield of carbon depositions and hydrogen yield in preliminary studies [37]. All the catalysts were then crushed and sieved to give granules in the size range of 0.05–0.18 mm. No reduction of the catalyst prior to the catalytic pyrolysis was carried out as the gases produced during pyrolysis-catalytic process such as H_2 and CO reduced the metal oxides in situ.

2.2. Experimental setup and procedure

The pyrolysis-catalysis of waste plastics was conducted in a two-stage fixed bed reactor as shown in Fig. 1. The experimental system consisted of a quartz tube reactor (I.D. 40 mm) with two temperature ranges (upper: pyrolysis zone, 310 mm height; lower: catalysis zone, 310 mm height), a gas supply system, gaseous product condensing system with ice and water mixture and a gas cleaning system followed by an off-line gas product, gas analysis system.

Three sets of experiment were carried out to determine the influence of process parameters on the production of hydrogen and carbon nanotubes; the effect of different catalyst type using Ni/γ-Al_2O_3, Ni/α-Al_2O_3, Fe/γ-Al_2O_3, Fe/α-Al_2O_3 and Ni-Fe/γ-Al_2O_3 catalysts; the influence of steam to plastic mass ratios of 0, 0.3, 1, 2.6; and catalytic temperatures of 700, 800, 900 °C. For each experiment, 0.5 g catalyst