Fuel Processing Technology 130 (2015) 46–53

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Influence of metal addition to Ni-based catalysts for the co-production of carbon nanotubes and hydrogen from the thermal processing of waste polypropylene

Mohamad Anas Nahil [1], Chunfei Wu [1], Paul T. Williams *,[1]

Energy Research Institute, The University of Leeds, Leeds LS2 9JT, UK

ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form 17 September 2014
Accepted 19 September 2014
Available online 12 October 2014

Keywords:
Waste
Reforming
Gasification
Plastic
Hydrogen
Carbon nanotubes

ABSTRACT

This paper investigates the co-production of hydrogen and carbon nanotubes from the pyrolysis–catalytic gasification of waste plastics (polypropylene). We report on the influence of a range of metal additions to a nickel based catalyst based on ternary mixed oxide types Ni–Metal–Al, where the metal was Zn, Mg, Ca, Ce or Mn. The results showed that of the different metal–nickel catalysts investigated, the Ni–Mn–Al catalyst was the most promising catalyst in relation to the co-production of hydrogen and CNT. For example, the Ni–Mn–Al catalyst produced 71.4 mmol hydrogen g^{-1} plastic, while the hydrogen production using Ni–Ca–Al, Ni–Ce–Al and Ni–Zn–Al catalysts were 68.5 mmol g^{-1}, 63.1 mmol g^{-1} and 45.9 mmol hydrogen g^{-1} plastic respectively. In addition, carbon deposition on the catalyst was highest in the order of: Ni–Mn–Al > Ni–Ca–Al > Ni–Zn–Al > Ni–Ce–Al > Ni–Mg–Al. The carbon deposition for the Ni–Mn–Al catalyst was found to consist of mostly carbon nanotubes. Further investigation of the Ni–Mn–Al catalyst demonstrated that the interaction between Ni and catalyst support plays a significant role in the gasification process; weak metal support interaction (for the Ni–Mn–Al catalyst calcined at 300 °C) resulted in a lower hydrogen production and much higher yield of carbon products. In addition, the influence of steam injection rate on hydrogen and carbon nanotube production was investigated for the Ni–Mn–Al catalyst. Increasing the steam injection rate significantly increased hydrogen production and decreased carbon deposition. However, at lower steam injection rates, the quality of the product carbon nanotubes was improved.

1. Introduction

Hydrogen is expected to become a promising energy carrier for sustainable energy consumption because it possesses high energy density (ca. 120.7 kJ/g) and its combustion produces no environmental pollutants [1–3]. Currently, hydrogen is industrially produced by the conversion of fossil fuels, which is considered as unsustainable and in addition, the process also releases greenhouse gases to the environment [4]. There is therefore great interest in producing hydrogen from alternative feedstocks. One such feedstock is waste plastic which can be thermally converted to hydrogen [5]. The world's overall consumption of plastics in 2010 was 230 million tonnes and the predictions are for an upward trend of 3% annual growth in plastics use in developed countries and 10% in developing countries [6]. The rapid rate of plastic consumption throughout the world has led to the creation of increasing amounts of plastic waste. For example, it is estimated that in Europe 25.2 million tonnes of plastic waste is generated each year [7].

The pyrolysis and gasification of waste plastic for hydrogen production have been extensively investigated [6,8–13]. Many catalysts have also been investigated to improve the efficiency of the process and to increase hydrogen production. Ni based catalysts have been reported to be effective for hydrogen production due to their high C–C bond breaking activity with significantly lower cost compared to noble metal catalysts such as Ru, Pt and Rh [14–16]. However, the main problem associated with Ni catalysts is that they suffer from a high deactivation rate caused by the formation of carbonaceous deposits. The deactivation involves covering of the catalyst active sites due to encapsulating by amorphous carbons; in addition carbon filaments and carbon nanotubes are also formed on the surface of the reacted catalyst [14,17,18].

Carbon nanotubes (CNTs) are a unique form of carbon due to their intrinsic properties such as extraordinary mechanical, electric, thermal stability and chemical inertness [19,20]. Therefore, production of higher quality CNTs at lower cost is of great importance. Different methods have been developed to produce CNTs including laser ablation [21], arc-discharge [22], chemical vapour deposition [23] and pyrolysis/catalytic steam reforming [24]. Chemical vapour deposition is considered as the most dominant method for CNT production, while gasification of waste plastics has received less attention. The main advantage of plastic

---

* Corresponding author.
E-mail addresses: m.a.nahil@leeds.ac.uk (M.A. Nahil), c.wu@leeds.ac.uk (C. Wu), p.t.williams@leeds.ac.uk (P.T. Williams).
[1] Tel.: +44 1133432504.

http://dx.doi.org/10.1016/j.fuproc.2014.09.022
0378-3820/

gasification in the presence of steam is that it can produce both CNT and also hydrogen depending on the conditions and the catalyst used. Currently, there are a few reports in relation to the simultaneous production of hydrogen and carbon nanotubes from waste plastics using thermochemical methods [25,26]. In order to increase the quality and quantity of CNTs, more work about catalyst development is needed.

Here, we investigate the influence of metal addition to Ni-based catalysts prepared by co-precipitation to determine their influence on the production of hydrogen and CNT from waste plastics as represented by waste polypropylene. Co-precipitation as a catalyst preparation method has drawn much attention due to its high catalytic effect on hydrogen production. It is well known that the stabilisation of Ni catalysts can be enhanced by the incorporation of the active metal into a mixed oxide matrix [27,28]. During the preparation of Ni based catalysts by co-precipitation, different cations can be introduced into the structure and will modify the catalytic properties, such as the particle morphology or metal reducibility in the final catalyst [28–30]. Accordingly, catalytic activity and stability will be directly related to the type of metals incorporated.

In this study, catalytic-steam reforming of waste plastic polypropylene was carried out to investigate the activity of Ni catalysts based on different types of ternary mixed oxides, Ni–Metal–Al, where the added metal was Zn, Mg, Ca, Ce or Mn. The catalysts were prepared by a co-precipitation method and their use in hydrogen and CNT production was investigated using a two stage fixed bed reactor. Metal addition to the Ni-based catalyst, water injection rate and interaction between Ni metals and catalyst support were studied.

2. Materials and methods

2.1. Materials

Waste plastic in the form of recovered waste polypropylene (PP) was obtained as 2 mm pellets provided by Regain Polymers Ltd., UK. A series of Ni based catalyst types Ni–Metal–Al (molar ratio 1:1:1) were prepared by a co-precipitation method using the rising pH technique according to the method reported by Garcia et al. [31]. The initial Ni–Metal–Al molar ratio was 1:1:1. As an example, Ni–Zn–Al catalyst was prepared starting with 200 ml of an aqueous solution containing $Ni(NO_3)_2\ 6H_2O$, $Zn(NO_3)_2\ 6H_2O$ and $Al(NO_3)_3\ 9H_2O$. The precipitant, 1 M NH_4OH, was added to this solution and the precipitation was carried out at 40 °C with moderate stirring until the final pH of 8.3 was obtained. The precipitates were filtered and washed with water (40 °C), followed by drying at 105 °C overnight, and then they were calcined at 750 °C for 3 h. The other catalysts Ni–Mg–Al, Ni–Ca–Al, Ni–Ce–Al and Ni–Mn–Al were synthesized following the same procedure described above, but replacing Zn nitrates by those of Mg, Ca, Ce and Mn, respectively. All the catalysts used in this paper were crushed and sieved to granules with a size of 65 to 212 μm. In addition, all the catalysts used were not reduced, reduction being carried out by the reducing gases such as hydrogen and carbon monoxide produced during the process.

2.2. Experimental pyrolysis–catalytic steam gasification system

Examination of the prepared Ni–Metal–Al catalysts for the purpose of hydrogen and CNT production from catalytic-steam reforming/gasification of waste polypropylene was carried out in a two-stage reaction system (Fig. 1). The two-stage fixed bed reaction system consisted of a first stage plastic pyrolysis and a second steam catalytic reforming/gasification stage. Approximately 2 g of waste polypropylene was pyrolysed in the first stage, and the pyrolysis products were passed directly to a second stage where steam catalytic reforming/gasification of the evolved pyrolysis gases was carried out. N_2 gas with a flow rate of 80 ml min^{-1} was used as carrier gas for each experiment and 1 g of the catalyst was used in the second stage.

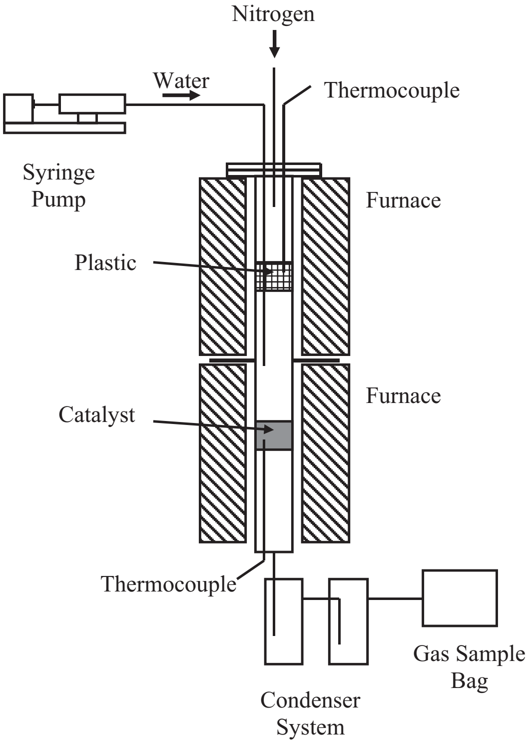

Fig. 1. Schematic diagram of the pyrolysis-reforming of waste plastic.

The experimental procedure consisted of initial heating of the catalyst in the second stage to 800 °C with a heating rate of 40 °C min^{-1}. Once the second catalyst stage reactor had stabilised at 800 °C, the waste plastic sample was then pyrolysed at a heating rate of 40 °C min^{-1} to the final pyrolysis temperature of 500 °C in the first stage reactor. The evolved pyrolysis volatiles were passed directly to the second stage where water was also introduced and thereby the pyrolysis volatiles were catalytically steam reformed/gasified. The water flow rate used was 4.74 g h^{-1}. Further work involving the Ni–Mn–Al catalyst investigated the influence of different steam flow rates on hydrogen and CNT formation at water injection rates of 0, 2.85, 4.74 and 8.54 g h^{-1}. Two condensers were used to trap the condensable products consisting of an air cooled condenser, followed by a solid CO_2 cooled condenser. The non-condensed gases were collected with a 25 L Tedlar TM gas sample bag. The gases collected in the sample bag were analysed off-line by packed column gas chromatography (GC). Hydrocarbon gases (C_1–C_4) were analysed using a Varian CP-3380 gas chromatograph with a Flame Ionisation Detector (FID) with a 80–100 mesh Hayesep column and nitrogen carrier gas. Carbon dioxide, hydrogen, nitrogen, carbon monoxide and oxygen were analysed with a separate Varian CP-3380 gas chromatograph fitted with two separate packed columns and with two thermal conductivity detectors (GC/TCD). Hydrogen, oxygen and carbon monoxide, methane and nitrogen were analysed on a 2 m length by 2 mm diameter column, packed with 60–80 mesh molecular sieve. Argon was used as the carrier gas. Carbon dioxide was analysed on a separate 2 m length by 2 mm diameter column with Hayesep 80–100 mesh packing material.

The calibration of the gas chromatograph was carried out prior to the analysis of gas samples obtained from the experiments. Precision standard gas mixtures including alkanes, alkenes and permanent gas mixture were used. In order to calculate the amount of gas in grams, the area obtained for each gas from gas chromatography was compared with the area of calibration gas, and the percentage of each gas in the mixture was calculated. As a known quantity of nitrogen was introduced into the reactor during the experiment and no nitrogen was produced from the experiment, the total gas volume could be calculated