Journal of Analytical and Applied Pyrolysis 125 (2017) 32–39

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Development of Ni- and Fe- based catalysts with different metal particle sizes for the production of carbon nanotubes and hydrogen from thermo-chemical conversion of waste plastics

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ARTICLE INFO

Keywords:
Hydrogen
Carbon nanotubes
Iron
Nickel
Catalyst

ABSTRACT

Co-production of valuable hydrogen and carbon nanotubes (CNTs) has obtained growing interest for the management of waste plastics through thermo-chemical conversion technology. Catalyst development is one of the key factors for this process to improve hydrogen production and the quality of CNTs. In this work, Ni/SiO_2 and Fe/SiO_2 catalysts with different metal particle sizes were investigated in relation to their performance on the production of hydrogen and CNTs from catalytic gasification of waste polypropylene, using a two-stage fixed-bed reaction system. The influences of the type of metals and the crystal size of metal particles on product yields and the production of CNTs in terms of morphology have been studied using a range of techniques; gas chromatography (GC); X-ray diffraction (XRD); temperature programme oxidation (TPO); scanning electron microscopy (SEM); transmission electron microscopy (TEM) etc. The results show that the Fe-based catalysts, in particular with large particle size (~80 nm), produced the highest yield of hydrogen (~25.60 mmol H_2 g^{-1} plastic) and the highest yield of carbons (29 wt.%), as well as the largest fraction of graphite carbons (as obtained from TPO analysis of the reacted catalyst). Both Fe- and Ni-based catalysts with larger metal particles produced higher yield of hydrogen compared with the catalysts with smaller metal particles, respectively. Furthermore, the CNTs formed using the Ni/SiO_2-S catalyst (with the smallest metal particles around 8 nm) produced large amount of amorphous carbons, which are undesirable for the process of CNTs production.

1. Introduction

Plastics are one of the most widely-used and multi-purpose materials. Due to increasing demand, global plastics production has continuously grown to 322 million tonnes in 2015, indicating a nearly 60% increase compared to the level in 1990 [1]. Recycling, energy recovery and landfill are the three main treatment options for plastics waste. At the moment, landfill is still largely used (~31 wt.%) in many EU countries, causing significant environmental problems and wasting the energy stored inside the plastics [2]. Therefore, converting waste plastics into valuable products e.g. hydrogen enriched syngas is promising as an alternative method for the management of waste plastics.

Hydrogen is a clean and efficient energy carrier and considered as an alternative fuel for the future. It is known that the use of catalysts is key to maximize the production of hydrogen during the thermo-chemical conversion process [3–6]. Many catalysts have been studied to improve hydrogen production from gasification of waste plastic. For example, Nanioka et al. [7] used Ru based catalysts to enhance hydrogen production from steam gasification of polystyrene using a fixed-bed reactor. A two-stage continuous reactor was used to optimize process conditions including reaction temperature and weight space velocity for gasification of polypropylene using Ru based catalysts [8]. In addition, Elordi et al. [9] used HZSM-zeolite with different ratios of SiO_2/Al_2O_3 as catalyst to investigate coke formation during hydrogen production from gasification of mixed plastics waste. However, it is known that noble-based catalysts are expensive for gasification of waste plastics. Cost effective Fe, Mo, Co and Ni supported on SiO_2, Al_2O_3, and MgO are effective catalysts for hydrogen production through hydrocarbon reforming reactions [10,11]. For example, high H_2 (29.1 wt%) yield was produced from polystyrene gasification by using Ni-based catalysts [12]. However, the formation of coke on the surface of catalysts and the problem of catalyst sintering are the two main challenges for the development of catalysts for the process. Ni catalysts supported on different metal oxides including Al_2O_3, ZrO_2, TiO_2, MgO and Ce_mO_2 and Cu/Mg/Al have been investigated with the aim to

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http://dx.doi.org/10.1016/j.jaap.2017.05.001
Received 23 January 2017; Received in revised form 29 March 2017; Accepted 2 May 2017
Available online 03 May 2017

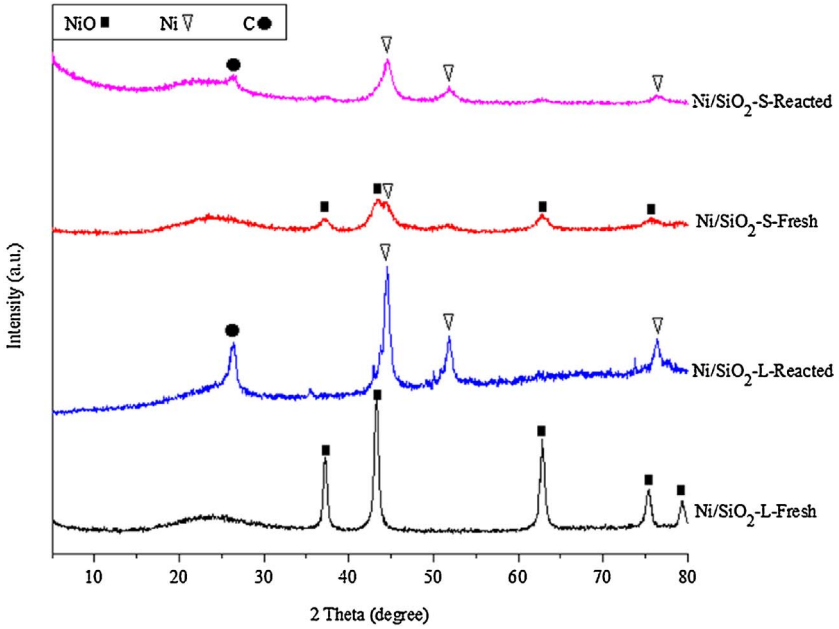

Fig. 1. XRD results for Ni-based catalysts before and after reaction.

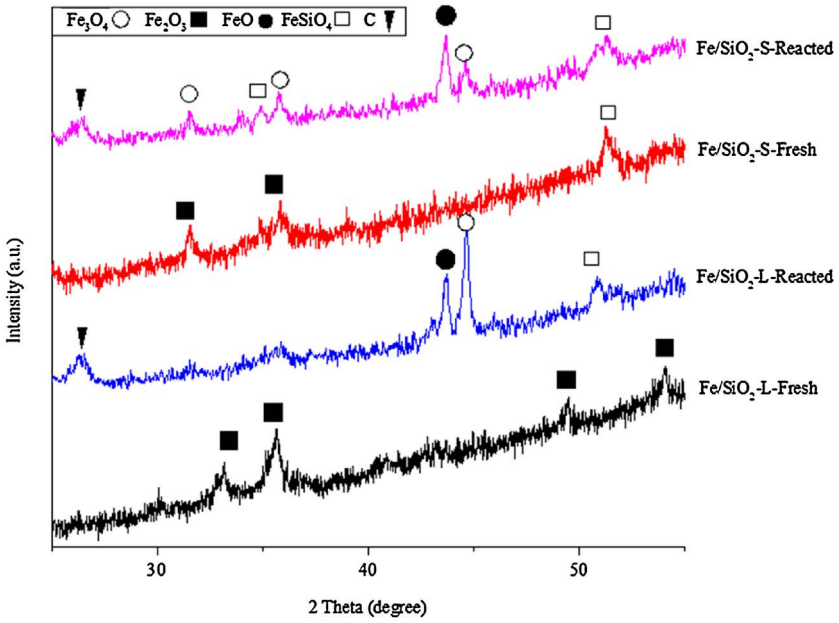

Fig. 2. XRD results for Fe-based catalysts before and after reactions.

reduce the formation of coke on the surface of the reacted catalyst [13–15].

In addition, several co-precipitated nickel-based catalysts have been investigated for hydrogen production from pyrolysis-gasification of polypropylene. Ni-Al (molar ratio 1:2) and Ni-Mg-Al (molar ratio 1:1:2) catalysts were found to show the most enhanced catalytic effectiveness in terms of H_2 production and the prevention of coke formation [16–18]. However, the formation of carbon on the reacted catalyst is largely un-avoidable. Producing carbon nanotubes (CNTs) together with hydrogen from waste plastics seems to be a promising development to maximize the economic feasibility of the process. CNTs are valuable materials having specific mechanical and electronic properties and has broad applications in the fields of energy and environmental protection [19,20].

Ni-Al catalysts doped with Ca and Zn have been investigated for the production of both hydrogen and CNTs from waste plastics [21]. Compared to Ni/Ca-Al catalyst, Ni/Zn-Al catalyst have been reported to produce higher yields of H_2, but with less production of CNTs, due to the promotion of catalytic interactions between steam and carbon containing compounds [16,21]. Zhao et al. [22] produced CNTs with uniform diameter and high quality using Ni-loaded catalysts from the reforming of ethanol. Ago et al. [10] synthesised CNTs with Ni and Fe-based catalysts supported by MgO using CH_4 as feedstock, and found that it was difficult to produce CNTs from Ni-based catalysts; they suggested that Ni-based catalysts had low metal diffusivity and carbon solubility.

The formation of CNTs depends on experimental parameters such as, catalyst particle size [23] and it has been suggested that the size of metal particles used in chemical vapor deposition could define the diameters of the CNTs growth [24]. For example, Baker et al. [25] and Kim et al. [26] reported that the growth of carbon nanotubes was governed by associated catalytic particles. However, there are few