Investigation of nickel-impregnated zeolite catalysts for hydrogen/syngas production from the catalytic reforming of waste polyethylene

Dingding Yao[a,b], Haiping Yang[a,*], Hanping Chen[a], Paul T. Williams[b,*]

[a] State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, 430074 Wuhan, China
[b] School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT UK

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ABSTRACT

Catalytic steam reforming of waste high density polyethylene for the production of hydrogen/syngas has been investigated using different zeolite supported nickel catalysts in a two-stage pyrolysis-catalytic steam reforming reactor system. Experiments were conducted into the influence of the type of zeolite where Ni/ZSM5-30, Ni/β-zeolite-25 and the Ni/Y-zeolite-30 catalysts were compared in relation to hydrogen and syngas production. Results showed that the Ni/ZSM5-30 catalyst generated the maximum syngas production of 100.72 mmol $g_{plastic}^{-1}$, followed by the Ni/β-zeolite-25 and Ni/Y-zeolite-30 catalyst. In addition, the ZSM-5 supported nickel catalyst showed excellent coke resistance and thermal stability. It was found that the Y type zeolite supported nickel catalyst possessed narrower pores than the other catalysts, which in turn, promoted coke deactivation of the catalyst. Large amounts of filamentous carbons were observed on the surface of the Ni/Y-zeolite-30 catalyst from scanning electron microscope images. In addition, the influence of Si:Al molar ratio for the Ni/ZSM-5 catalysts in relation to hydrogen and syngas yield was investigated. The results indicated that hydrogen production was less affected by the Si:Al ratio than the type of zeolite support. Also, the Ni/ZSM5-30 catalyst was further investigated to determine the influence of different process parameters on hydrogen and syngas yield via different reforming temperatures (650, 750, 850 °C) and steam feeding rate (0, 3, 6 g h^{-1}). It was found that increasing both the temperature and steam feeding rate favoured hydrogen production from the pyrolysis-catalytic reforming of waste polyethylene. The optimum catalytic performance in terms of syngas production was achieved when the steam feeding rate was 6 g h^{-1} and catalyst temperature was 850 °C in the presence of Ni/ZSM5-30 catalyst, with production of 66.09 mmol H$_2$ $g_{plastic}^{-1}$ and 34.63 mmol CO $g_{plastic}^{-1}$.

1. Introduction

Hydrogen is an environmentally-friendly and efficient clean energy with the attraction that its combustion only releases water and energy [1]. Hydrogen production from waste resources such as waste plastics and biomass instead of fossil fuels appears to be more favourable as it overcomes the environmental impact resulting from the over-exploitation of non-renewable resources [2,3]. In addition, considerable amounts of waste plastics are generated each year which a considerable proportion are landfilled, resulting in a waste of resource [4]. Therefore, the production of hydrogen from waste plastics represents an attractive technology for energy recycling in terms of waste management as well as the sustainable ecosystem.

Waste plastics can be thermally converted into hydrogen by pyrolysis-gasification/reforming. A two-stage reaction system was reported by Wu and Williams [5] where pyrolysis of the plastics was followed by catalytic steam reforming of the pyrolysis gases and where the

hydrogen production could be optimised by manipulating the process parameters of the two separate processes. The investigation of catalyst promoters and calcination temperature were also carried out to improve the hydrogen production [6]. Barbarias et al. [7] used a two stage spouted-fluidized bed reactor for the continuous production of hydrogen from high density polyethylene in relation to process conditions. Dou et al. [8] optimized hydrogen production from waste plastics by integrating the gasification of the plastics with a sorption-enhanced steam reforming system, where up to 88.4 vol.% of H$_2$ gas concentration was achieved. The feasibility of the two-stage system for hydrogen production was also demonstrated by Czernik et al. [9], where a hydrogen yield of 34 g per 100 g polypropylene was obtained for a 10 h duration test.

Various catalysts have been investigated for hydrogen and syngas production from waste plastics. Ru-based catalysts were prepared by Namioka et al. [10] and Park et al. [11] to catalyse the gasification/reforming of municipal waste plastics, and were found to be effective to

compensate for feedstock compositional variations. Currently, nickel is the most commonly used catalyst metal for thermal conversion of hydrocarbons due to its effective activity and lower cost [12]. Mg modified Ni based catalysts have been studied to investigate different operational parameters for hydrogen production and to minimise coke formation during the pyrolysis-catalytic reforming of plastics [13]. Vizcaino et al. [14] suggested the Ni was the phase responsible for enhanced hydrogen production using bimetallic catalysts.

The catalyst support is also important in relation to the activity of the Ni based catalysts. The agglomeration of Ni particles can easily occur in the absence of support, leading to reduction in the catalyst activity [15,16]. Therefore, it is of interest to prepare well-dispersed Ni catalysts using a porous support material. Zeolite catalysts are crystalline, alumina-silicates with an open structure consisting of AlO_4 and SiO_4 tetrahedral crystal structure with a defined pore size and defined microporous structure. Zeolites could provide the porous support material for nickel to aid metal dispersion and enhance catalytic activity for the production of hydrogen-rich syngas. For example, Teh et al. [17] reported that Ni on a ZSM-5 support enhanced the catalytic activity of the catalyst which was attributed to the presence of micro–-mesoporosity and basicity which produced a synergistic effect. The introduction of Ni into the ZSM5 structure has also been suggested to reduce catalyst coke formation by reducing the strong Bronsted acidity of ZSM5, which provide the major active sites for coke formation [18].

The investigations of Ni/zeolite for waste thermal conversions have been investigated by several researchers. Nickel-impregnated ZSM-5 catalysts were prepared and tested by Yung et al. [19] for the upgrading of biomass pyrolysis vapours, where the effects of Ni pre-treatment method and loading were discussed. Karnjanakom et al. [20] reported high catalyst activity and long-term stability of a Ni/MCM-41-EG catalyst for biomass derived tar reforming. Ni based or porous zeolites have also been studied extensively for the catalytic pyrolysis of waste plastics [21–23]. However, there are few detailed researches on hydrogen rich syngas production from waste plastics using different Ni based porous supports such as zeolite. In this paper, different zeolites (ZSM-5, Y-zeolite and β-zeolite) were used as catalyst supports for Ni for the pyrolysis-catalytic steam reforming of waste high density polyethylene (HDPE). The investigation of hydrogen and carbon monoxide yield in relation to zeolite type and Si:Al molar ratio were conducted. In addition, the influence of operational parameters including catalyst reforming temperature and steam feeding rate were also investigated to optimize the syngas production.

2. Materials and methods

2.1. Feedstock and catalyst

High density polyethylene was supplied as recycled waste plastic as 2–3 mm sized pellets by Regain Polymers Limited, Castleford, UK. The ultimate analysis of the plastic feedstock was determined using a Vario Micro Elemental Analyzer, and the elemental content was 84.86 wt.% carbon, 13.64 wt.% hydrogen, 0.98 wt.% oxygen, 0.03 wt.% nitrogen and 0.14 wt.% sulphur. High density polyethylene would not be expected to contain oxygen, nitrogen or sulphur, however, the plastic was a 'real-world' recycled plastic and contained some contamination, possible from other types of plastic. The zeolites used for the pyrolysis-catalytic steam reforming of the waste plastic were purchased from Alfa Aesar and were; ZSM5-30 (ammonium form, Si:Al molar ratio 30, surface area 400 $m^2 g^{-1}$); ZSM5-50 (ammonium form, Si:Al molar ratio 80, surface area 425 $m^2 g^{-1}$); ZSM5-80 (ammonium form, Si:Al ratio 80, surface area 425 $m^2 g^{-1}$); β-zeolite-25 (ammonium form, Si:Al ratio 25, surface area 680 $m^2 g^{-1}$); Y-zeolite-30 (hydrogen from, Si:Al ratio 30, surface area 780 $m^2 g^{-1}$). The ammonium forms of the zeolite support were pre-treated at 450 °C in a muffle furnace under static air for 6 h (with a heating rate of 5 °C min^{-1}) to obtain the protonic form [24].
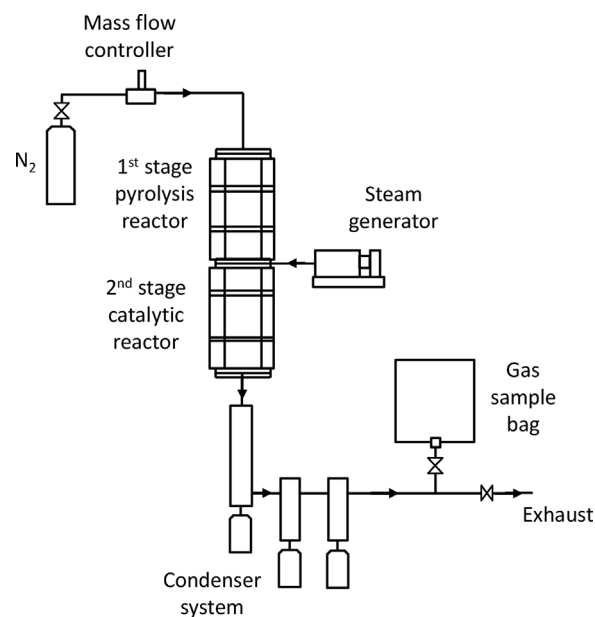
Ni introduction into the zeolite support was achieved by an

Fig. 1. Schematic diagram of the reactor system for the pyrolysis-catalytic steam reforming of waste plastic.

impregnation method, 5.50 g Ni(NO$_3$)$_2$·6H$_2$O (purchased from Sigma-Aldrich) was completely dissolved into 20 ml ethanol solution, followed by addition of 10 g of the zeolite support so that a Ni loading of 10 wt.% was obtained. The solution was then stirred using a magnetic stirrer at 60 °C to produce a slurry. The precursor slurry was dried overnight and calcined at 500 °C for 3 h (heating rate of 10 °C min^{-1}). The catalyst was then pressed and sieved to obtain particles sizes between 50–212 μm.

2.2. Experimental reactor system and procedure

A schematic diagram of the experimental apparatus for the pyrolysis-catalytic steam reforming of waste HDPE is shown in Fig. 1. The reaction system consisted essentially of a steam feeding system with a water syringe pump, a two-stage stainless steel tube reactor, an inert gas supply system, gaseous product condensing system and gas measurement system. The reactor was externally electrically heated and had two separate heating zones, i.e. first stage plastic pyrolysis reactor of 200 mm height and 40 mm i.d.; second stage catalytic reactor of 300 mm height and 22 mm i.d. The temperatures of the two zones were monitored and controlled separately. In order to explore the effect of different Ni/zeolites on the pyrolysis-catalytic reforming of waste HDPE, two sets of experiment were conducted: the influence of Si:Al ratio of the zeolite support and the influence of zeolite structure type on the yield of hydrogen and syngas. For each experiment, 1 g of waste HDPE and 0.5 g of catalyst were placed in the pyrolysis and reforming stages, respectively. The second catalytic stage was preheated to the catalyst temperature of 850 °C, except where the influence of temperature was investigated, where pre-heating was to 650, 750 or 850 °C. Once the second stage catalyst reactor had reached the desired temperature, the first pyrolysis stage was then heated from room temperature to 500 °C at 40 °C min^{-1} to generate the pyrolysis gases for reforming. In addition, water was injected into the second stage with a flow rate of 6 ml h^{-1} for the catalytic steam reforming process. High purity nitrogen was supplied as inert gas. The condensable liquids were collected in the condensers which were cooled by dry ice, and the non-condensable gases were collected in a 25 l Tedlar™ gas sample bag for gas chromatography (GC) analysis. The total experimental time was around 30 mins. All experiments were repeated to ensure the reliability of the results.