



Catalytic processing of non-condensable pyrolysis gas from plastics: Effects of calcium supports on nickel-catalyzed decomposition of hydrocarbons and HCl sorption

Andrei Veksha^{a,*}, Apostolos Giannis^a, Wen-Da Oh^{a,b}, Grzegorz Lisak^{a,c,*}

^a Residues and Resource Reclamation Centre (R3C), Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Clean Tech One, 637141, Singapore

^b School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

^c School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

HIGHLIGHTS

- Catalytic upgrading of non-condensable pyrolysis gas from plastics was studied.
- CaCO_3 , $\text{Ca}(\text{OH})_2$, CaO and their mixtures were used as supports for Ni.
- All catalytic sorbents can remove HCl from non-condensable pyrolysis gas.
- Ca support influences on hydrocarbon decomposition and carbon formation.
- Catalytic activity was related to porous properties of catalytic sorbents.

ARTICLE INFO

Article history:

Received 27 February 2018

Received in revised form 29 May 2018

Accepted 4 June 2018

Available online 4 June 2018

Keywords:

Calcium support
Catalytic decomposition
HCl sorption
Hydrocarbons
Plastics
Pyrolysis gas

ABSTRACT

Non-condensable pyrolysis gas is a suitable source of hydrocarbons for energy applications. The purpose of this study was to develop a catalytic process for selective decomposition of unsaturated hydrocarbons in the pyrolysis gas as these species compromise the operation of gas engines, gas turbines and fuel cells. The effect of different calcium supports, namely CaCO_3 , $\text{Ca}(\text{OH})_2$, CaO and their mixtures, on the performance of Ni-based catalytic sorbents during the decomposition of hydrocarbons and HCl sorption from non-condensable pyrolysis gas of mixed plastics was investigated. The plastic mixture containing low density polyethylene (40%), polypropylene (40%), polystyrene (10%) and polyvinyl chloride (10%) was initially pyrolyzed at 600 °C producing condensable oils and non-condensable gases. The non-condensable gases were further treated in a subsequent reactor at 700 °C in the presence of catalytic sorbents. All catalytic sorbents were effective for HCl sorption, decreasing the HCl concentration in the gas stream below detectable levels. However, the choice of calcium support had a substantial effect on the catalytic decomposition of hydrocarbons and the properties of produced carbon deposits. CaCO_3 , $\text{Ca}(\text{OH})_2$ and their mixture at 1:1 ratio by mass loaded with Ni showed higher catalytic activity towards the decomposition of hydrocarbons compared to CaO and a mixture containing CaO , CaCO_3 and $\text{Ca}(\text{OH})_2$ at 1:1:1 ratio by mass. Furthermore, carbon deposits produced on the surface of Ni supported on CaCO_3 , $\text{Ca}(\text{OH})_2$ and their mixture contained multi-walled carbon nanotubes, whereas carbon deposits produced on Ni supported on CaO and the mixture containing CaO had non-filamentous morphology. The observed results can be attributed to the low BET specific surface areas and pore volumes of CaO -containing catalytic sorbents which could limit the dispersion of Ni resulting in low catalytic activity.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Plastic waste is an abundant source of hydrocarbons for energy recovery, production of petrochemicals and chemical synthesis. In this respect, pyrolysis technology that involves the decomposition of solid feedstock in the absence of air is gaining an increasing

* Corresponding authors at: Residues and Resource Reclamation Centre (R3C), Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Clean Tech One, 637141, Singapore (A. Veksha, G. Lisak).

E-mail addresses: aveksha@ntu.edu.sg (A. Veksha), g.lisak@ntu.edu.sg (G. Lisak).

attention due to its suitability to process mixed plastics, which is challenging using other technologies. Commercial pyrolysis plants with capacities of several thousand tonnes per year are in operation (Scheirs et al., 2006; Butler et al., 2011), demonstrating high maturity level of the technology. Pyrolysis process allows the conversion of complex mixture of plastics (including polyvinyl chloride, polyethylene terephthalate, acrylonitrile and nylon) into liquid fuel (main product) that is used either without further treatment or after refining (Scheirs et al., 2006; Butler et al., 2011; Kaimal and Vijayabalan, 2015; Miandad et al., 2016; Al-Salem et al., 2017; Lopez et al., 2017).

Non-condensable pyrolysis gas from plastics accounts for 10–90% of plastic feed, depending on the process design and operating conditions (Butler et al., 2011; Lopez et al., 2017; Aguado et al., 2008; Wong et al., 2015). This gas is typically burnt at industrial scale to provide heat for the process (Scheirs et al., 2006; Butler et al., 2011). Previous research has demonstrated that the non-condensable pyrolysis gas is suitable for the production of high-value carbon based nanomaterials that can increase economic viability and diversify revenue streams of pyrolysis plants (Liu et al., 2011; Arnaiz et al., 2013; Aboul-Enein et al., 2017; Veksha et al., 2017). Furthermore, owing to the high calorific value, non-condensable pyrolysis gas from plastics can replace natural gas as a fuel (Honus et al., 2016). The removal of unsaturated hydrocarbons from non-condensable pyrolysis gas is required, as these compounds cause coking, polymerization and soot formation in the downstream equipment (Glaude et al., 2005; Lefebvre and Ballal, 2010; Speight, 2011; Pomfret et al., 2008). Previously, we have successfully utilized Ni supported on CaCO_3 for the catalytic upgrading of non-condensable pyrolysis gas from plastics (Veksha et al., 2018). Ni/ CaCO_3 plays dual role in this process. Both Ni and CaCO_3 contribute to the decomposition of unsaturated hydrocarbons containing in the gas stream. Additionally, CaCO_3 acts as a sorbent for HCl released from polyvinyl chloride, a common component in the mixed plastic waste. The end-product gas is HCl free and has the composition similar to reformat fuels suitable for solid oxide fuel cells. Thus, the application of Ni/ CaCO_3 as a catalytic sorbent allows the energy recovery at the plastic pyrolysis plants.

Besides CaCO_3 , other calcium compounds, such as CaO and $\text{Ca}(\text{OH})_2$ have high HCl sorption capacity. Compared to MgO and $\text{Mg}(\text{OH})_2$, CaO and $\text{Ca}(\text{OH})_2$ demonstrated higher HCl removal efficiencies during polyvinyl chloride pyrolysis (Wootthikanokkhan et al., 2003). Furthermore, the calcium compounds have low toxicity compared to, for instance, barium species suitable for dechlorination of gas streams (Wang et al., 2017). The suitability of CaO and $\text{Ca}(\text{OH})_2$ as supports of catalytic sorbents that can simultaneously remove HCl and decompose hydrocarbons containing in pyrolysis gases has not been investigated. The purpose of this study is to evaluate the efficiency of catalytic sorbents prepared from different calcium supports (CaCO_3 , $\text{Ca}(\text{OH})_2$, CaO and their mixtures) loaded with nickel towards the decomposition of non-condensable pyrolysis gas with simultaneous HCl removal. The effects of calcium supports on the HCl sorption, conversion of hydrocarbons, carbon deposition and gas evolution are addressed.

2. Materials and methods

2.1. Materials

The catalytic sorbents were prepared by impregnation method using calcium carbonate (Reagent and Fine chemicals, >98.5%), calcium hydroxide (Sigma-Aldrich, >96%), calcium oxide (Alfa-Aesar, >98%) and nickel nitrate hexahydrate (Sigma-Aldrich, >97%). All chemicals for the preparation of catalytic sorbents were used as

received. 5 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in ethanol and 19 g of CaCO_3 , $\text{Ca}(\text{OH})_2$, CaO or mixtures of these compounds were added to the solution. Specifically, two mixtures of calcium compounds were used, namely CaCO_3 , $\text{Ca}(\text{OH})_2$ and CaO in a 1:1:1 ratio by mass (denoted as CaMix-1) and CaCO_3 and $\text{Ca}(\text{OH})_2$ in a 1:1 ratio by mass (denoted as CaMix-2). The solvent was evaporated in a rotary evaporator Hei-Vap Precision (Heidolph Instruments) at 50 °C under 100 mbar vacuum. After impregnation, the materials were dried overnight in an oven at 55 °C and then calcined in air at 750 °C for 3 h (heating rate 2 °C min^{-1}). The calcined materials were sieved to obtain the particles with sizes 63–212 μm . The sample names were denoted as xNi/support, where “x” is a mass percent of Ni loading in the catalytic sorbent and “support” is CaCO_3 , $\text{Ca}(\text{OH})_2$, CaO, CaMix-1 or CaMix-2.

2.2. Experimental procedure

The experiments were conducted in a setup comprising of two reactors (Fig. S1, Supplementary data) (Veksha et al., 2018). The horizontal quartz reactor (i.d. 53 mm) was used for pyrolysis of plastic mixture. For each experimental run, pure polymers were used to prepare a plastic mixture comprising of 0.75 g of low density polyethylene (LDPE) from PTT Global Chemical Public Co. Ltd. (Thailand), 0.75 g of polypropylene (PP) from Sinopec (China), 0.18 g of polystyrene (PS) from Formosa Plastics Corp. (Taiwan) and 0.18 g of polyvinyl chloride (PVC) from Hop Fu Plastics Ltd. (China). The produced volatiles passed through a condenser at ambient temperature to remove condensable hydrocarbons. The non-condensable gas was transferred to the vertical quartz reactor (i.d. 17 mm) containing catalytic sorbent for the decomposition of hydrocarbons and HCl sorption. A known mass of catalytic sorbent was loaded into the vertical reactor. Approximately 200 mL of NaOH (0.025 M) was used in the HCl trap. The catalytic sorbent in the vertical reactor was heated at 15 °C min^{-1} to 700 °C in a N_2 flow (100 mL min^{-1}). Once the desired temperature was reached, the plastic mixture in the horizontal reactor was heated at 10 °C min^{-1} to 600 °C and pyrolyzed for 0.5 h. The produced non-condensable pyrolysis gas passed through the vertical reactor with the catalytic sorbent for the decomposition of hydrocarbons and HCl removal. In the flow of hydrocarbons and H_2 produced during the decomposition process, NiO was reduced to metallic Ni (Liu et al., 2011). Therefore, no reduction of catalyst prior to the decomposition of hydrocarbons was required. The evolved gas from the vertical reactor was collected in a gas bag and analyzed using a calibrated gas chromatograph equipped with a flame ionization detector for hydrocarbons (C_1 – C_5) and two thermal conductivity detectors for N_2 , O_2 , CO, CO_2 , and H_2 analysis (7890B model, Agilent Technologies Inc.). Since the formation of coke and oil/wax during plastic pyrolysis was extensively covered in previous studies (Scheirs et al., 2006; Butler et al., 2011; Kaimal and Vijayabalan, 2015; Miandad et al., 2016; Al-Salem et al., 2017; Lopez et al., 2017; Aguado et al., 2008; Wong et al., 2015), only the quantification and analysis of non-condensable pyrolysis products were carried out in this study. The volumes of gases produced from plastic pyrolysis were calculated based on the concentrations determined by the gas chromatograph and a known volume of N_2 carrier gas measured by the mass flow meter with totalizer installed before the horizontal reactor. The content of HCl captured in the NaOH trap was quantified by ion chromatography (Dionex ICS-1100, Thermo Scientific). The decomposition of hydrocarbons and HCl sorption were calculated from the differences between the contents of these compounds (i.e. volumes of hydrocarbons measured by gas chromatography and total HCl contents measured by ion chromatography) after the heat treatment of pyrolysis gas in the absence and presence of catalytic sorbents. All experiments were triplicated.

Download English Version:

<https://daneshyari.com/en/article/6588349>

Download Persian Version:

<https://daneshyari.com/article/6588349>

[Daneshyari.com](https://daneshyari.com)