Journal of Analytical and Applied Pyrolysis 125 (2017) 296–303

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Sulphated zirconia catalysed conversion of high density polyethylene to value-added products using a fixed-bed reactor

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ARTICLE INFO

Article history:
Received 9 December 2016
Received in revised form 4 March 2017
Accepted 18 March 2017
Available online 24 March 2017

Keywords:
Plastic waste
HDPE
Sulphated zirconia
Fixed-bed reactor
TGA
Catalytic conversion

ABSTRACT

A sulphated zirconia catalyst (SZ) was investigated for catalytic conversion of high density polyethylene (HDPE) to liquid and gaseous hydrocarbons using a fixed-bed reactor. The SZ catalyst reduced the onset of degradation from 337 °C for HDPE alone to 187 °C with 10 wt% SZ added. At 450 °C a complete weight loss was obtained with the SZ addition against only 4 wt% loss for HDPE only. Fixed-bed reactor experiments using 2 g of HDPE with 10 wt% SZ catalyst with a 30 min residence time showed a 98.0 wt% conversion at temperature as low as 380 °C. The liquid yield obtained was 39.0 wt% with a composition of 16 wt% paraffins, 21 wt% olefins, 5 wt% naphthenes and 58 wt% aromatics. The carbon number distribution of the liquid was C7–C12, which is within the gasoline range. Equally, gaseous products ranging from methane up to different isomers of pentane which contained more paraffinic and naphthenic hydrocarbon were obtained. The sulphated zirconia catalyst was found to have high ammonia desorption (337.0 μmol NH_3 g^{-1}), BET surface area (116.0 m^2 g^{-1}), external surface area (112.0 m^2 g^{-1}) and mesoporous structure. The overall results indicate that sulphated zirconia had excellent properties for catalytic conversion at temperature as low as 380 °C with significant liquid yield which could offer a solution to plastic waste problem by converting the waste back into value-added chemicals and fuel.

1. Introduction

Catalytic conversion using heterogeneous catalyst has been identified as a potential option to convert plastic waste back into useable fuels and raw materials for the chemical industry [1–5]. A range of heterogeneous catalysts have been investigated, including zeolites (HZM-5, HUSY, HMOR), both fresh and spent FCC-based zeolites, MCM-41 and various silica-alumina systems and clay-based catalysts [3,6–19]. A common feature of the catalysts used is conversion at temperatures above 450 °C to generate primary gaseous species that can then enter the pore-space of the catalysts where the secondary reactions take place for producing the end products. Sulphated zirconia (SZ), or so-called super solid catalyst, has the potential to promote primary cracking of the polymer into oligomers at temperatures below 450 °C and has thus been used as an excellent catalyst for oil refining processes, such as cracking and isomerisation [20–24]. Hence, SZ could be used during plastic waste conversion to promote conversion into short chain liquid and gaseous species at temperatures below 450 °C and may pave the way for a system to depolymerise ethylene-based polymers into liquids in the gasoline or diesel boiling point range.

The excellent activity of sulphated zirconia catalyst is traced to its super acidity composed of Brönsted and Lewis acid sites, large surface area, mesoporosity, thermal and chemical stability and simplicity in preparation [25]. The inductive effect of the S=O group from SO_4^{2-} in sulphated zirconia creates electronic deficiency that promote the Lewis acidity of Zr cation and thus promotes its acidity to super acidity. Sulphated zirconia has been reported to possess exceptional catalytic properties that could promote effective conversions of hydrocarbons to highly branched alkanes with high octane number at low temperature, where its catalytic structure and activity can be tailored by calcination [24]. It has been studied for many years and reported to be a very effective catalyst used in catalysing many processes in the oil refining and petrochemical industries [41,42]. Apart from alkane isomerisation, sulphated zirconia was also reported to be very efficient catalyst in many important processes, namely, hydrocracking, alkylation, condensation, esterification, acylation, oligomerisation and many organic synthesis reactions [21,22,26–31]. Sulphated zirconia with the aforementioned properties may offer an excellent catalytic activity in converting plastic, which is naturally viscous and has

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http://dx.doi.org/10.1016/j.jaap.2017.03.013
0165-2370/

Table 1
Physicochemical composition of the HDPE sample used in this work.

Sample	Proximate analysis (dry) wt%			Elemental composition (%)				
	Volatile matter	Ash	Fixed carbon	C	H	N	O	S
HDPE	96.83	0.00	3.17	85.7	14.1	0.00	0.00	0.00

bulky structure. The use of sulphated zirconia for plastic conversion has not been reported to the best of best of the authors' knowledge and could pave way for low temperature and tailored conversion of plastic waste into valuable liquid streams.

This work is aimed at evaluating sulphated zirconia catalyst for the conversion of high density polyethylene (HDPE) into value-added hydrocarbon products. This study also examines effect of temperature on product yields and in particular liquid product which could be used as fuel or industrial raw materials. The main focus is to find the applicability of sulphated zirconia in converting plastic waste to hydrocarbon products with gasoline range compositions at low temperature. Hence, developing a possible method for plastic waste recycling that is sustainable and cost-effective using sulphated zirconia catalyst.

2. Experimental

2.1. Materials

High density polyethylene 3 mm pellets (HDPE, Sigma–Aldrich, UK) with a density of 0.952 g/mL, melt index of 42 g/10 min with 99.9% purity were grounded to 0.05–0.25 mm using an SM2000 Retch Milling Machine. Table 1 lists the proximate and elemental compositions of the HDPE using a Thermo Scientific Flash Elemental Analyser (Flash EA, 1112 series). A 7 mol% SO_3 solid acid sulphated zirconia catalyst with a 100–150 μm particle size range was supplied by MEL chemicals, UK. The catalyst was calcined in air for 4 h at 550 °C using a Maffle furnace, cooled and kept in desiccators prior to use.

2.2. Catalyst characterisations

Surface morphology and elemental/oxide composition of the catalyst were analysed using a FEI QUANTA 600F scanning electron microscopy (SEM) version 2.4 coupled with a Genesis spectrum version 5.21 EDX analyser. Powder X-ray diffraction (XRD) patterns were obtained using a Hiltonbrooks DG 3 operated at 40kv with a 20 mA Philips PW 1050 goniometer, proportional detector and monochromatic Cu K_β radiation. The scanning was carried out at a scan speed of 2° (2θ) min^{-1} across a range 5–65° with a step size of 0.05°. A Micrometrics Gemini VII 2390 V3.03 surface area/porosity analyser was used to measure the BET surface area of the catalyst under nitrogen adsorption. The ammonia temperature programmed desorption (TPD) was carried out using a Quantachrome ChemBET TPR/TPD instrument, which was fitted with a TPRWin version 3.5 software for data analysis. Approximately 0.5 g of the catalyst sample was degassed for 30 min at 250 °C under helium, cooled to 50 °C and exposed to 30 mL min^{-1} ammonia gas for 10 min. Weakly physisorbed ammonia was purged with helium for 30 min before the TPD analysis from 50 °C to 700 °C with a heating rate of 10 °C min−1.

2.3. Analysis

The TGA analysis was conducted in duplicates under nitrogen using a Perkin-Elmer Pyris1 thermogravimetric analyser (TGA1) at 10 °C min^{-1} from 35 to 900 °C on 20 mg. The liquid products obtained from the fixed-bed reactor outlined in Section 2.4 were diluted with 9 parts DCM and analysed using a Variant CP-3800 Gas Chromatograph interfaced to a 1200 Quadrupole mass spectrometer with an ionising energy of 70 eV, source temperature of 280 °C and a VF-1MS fused silica capillary column (50 m × 0.32 mm i.d.) coated with BPX5 (0.25 μm film thickness). Helium was employed as the carrier gas and a programme temperature was set at 50 °C for 2 min, then increased to 300 °C at a heating rate of 5 °C min^{-1} and remained there for 30 min. The gaseous products from the fixed-bed reactor outlined in Section 2.4 were analysed using a Perkin Elmer Clarus 580 Gas Chromatograph (GC) fitted with both a Flame Ionisation Detector (FID) and a thermal conductivity detector (TCD) both operating at 200 °C. About 5 μL of the gas sample was injected with helium as the carrier gas and held at 60 °C and remained for

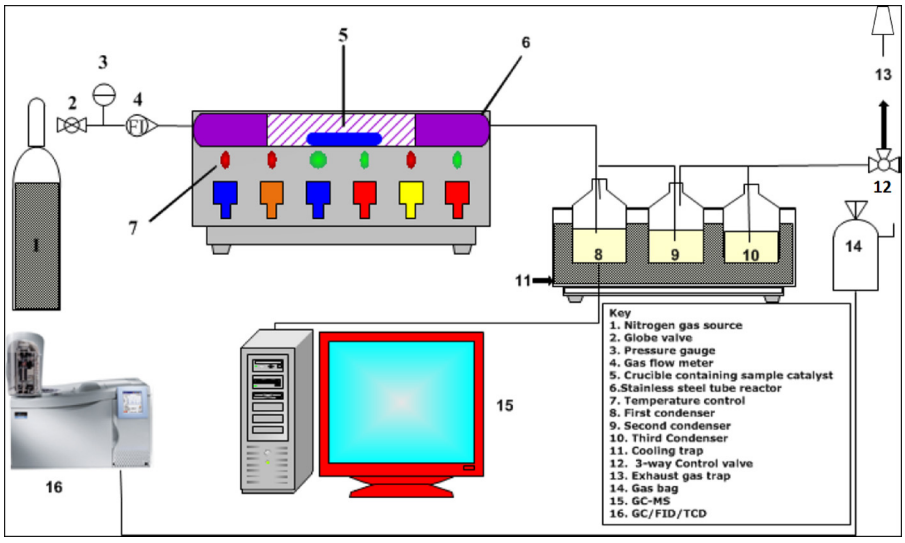

Fig. 1. Schematic diagram of a fixed bed reactor set-up for the for HDPE catalytic conversion.