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Catalytic pyrolysis of polyolefin waste into valuable hydrocarbons over reused catalyst from refinery FCC units

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Abstract

A commingled polyethylene/polypropylene (PE/PP) mixture was pyrolysed over used fluid catalytic cracking (FCC) commercial equilibrium catalyst (RCat-c1) using a laboratory fluidised-bed reactor operating isothermally at ambient pressure. The conversion at 390 °C for RCat-c1 catalyst (81.5 wt%) gave much higher yield than silicate (only 18.3 wt%). Greater product selectivity was observed with RCat-c1 as a post-use catalyst with about 53 wt% olefins products in the C_3–C_6 range. The selectivity could be further influenced by changes in reaction conditions. Valuable hydrocarbons of olefins and *iso*-olefins were produced by low temperatures and short contact times used in this study. It is demonstrated that the use of spent FCC commercial catalyst and under appropriate reaction conditions can have the ability to control both the product yield and product distribution from polymer degradation, potentially leading to a cheaper process with more valuable products.

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1. Introduction

Polymer waste can be regarded as a potential source of chemicals and energy. Methods for recycling polymer waste have been developed and new recycling approaches are being investigated [1]. The production of liquid hydrocarbons from polymer degradation would be beneficial in that liquids are easily stored, handled and transported. However, these aims are not easy to achieve. An alternative strategy is that of chemical recycling, known as feedstock recycling or tertiary recycling, which has attracted much interest recently with the aim of converting waste polymers into basic petrochemicals to be used as chemical feedstock or fuels for a variety of downstream processes [2]. The most widely used conventional chemical methods for waste polymer treatment are pyrolysis and catalytic reforming. Since thermal degradation demands relatively high temperatures and its products require further processing for their quality to be upgraded, catalytic degradation of polymer waste offers considerable advantages. Suitable catalysts have the ability to control both the product yield and product distribution from polymer degradation as well as to reduce significantly the reaction temperature [3–5].

Some polymeric materials, e.g., polystyrene, can be decomposed thermally in high yields to the monomers. However, this is not true for polyethylene (PE) or polypropylene (PP), which are among the most abundant polymeric waste materials typically making up 60–70% of municipal solid waste. It would be desirable to convert these waste polyolefins into products of value other than the monomers, because the products could be of sufficient value to offset the collection and pyrolysis costs. Studies of the effects of catalysts on the catalytic degradation of polymer has been performed by contacting melted polymer with catalyst in fixed bed reactors [6–8], heating mixtures of polymer and catalyst powders in reaction vessels [9–11] and passing the products of polymer pyrolysis through fixed bed reactors containing cracking catalysts [12–14]. Catalytic pyrolysis has been carried out by considering a variety of catalysts with little emphasis on the reactor design, with only simple adiabatic batch and fixed bed reactors being used. However, the configuration of the pyrolysis-reforming reactors poses serious engineering and economics constraints. The use of fixed beds or adiabatic batch where polymer and catalyst are contacted directly leads to problems of blockage and difficulty in obtaining intimate

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contact over the whole reactor. Without good contact the formation of large amounts of residue are likely, and scale-up to industrial scale is not feasible. Therefore, a fluidised-bed reactor has been used to study catalytic cracking of polymer waste by limiting the contact between primary volatile products and the catalyst/polymer mixture [15–18].

The catalytic degradation of polymeric materials has been reported for a range of catalysts centred around the active components in a range of different model catalysts, such as amorphous silica–aluminas, zeolites Y, ZSM-5 and various acidic catalysts and particularly the new family of MCM materials [6–18]. However, these catalysts have been used that even if performing well, they can be unfeasible from the point of view of practical use due to the cost of manufacturing and the high sensitivity of the process to the cost of the catalyst. An economical improvement of processing the recycling via catalytic cracking would operate in mixing the polymer waste with fluid catalytic cracking (FCC) commercial catalysts. These catalysts increase significantly the commercial potential of a recycling process based on catalytic degradation, as cracking catalysts could cope with the conversion of plastic waste co-fed into a refinery FCC unit [19–21]. Therefore, a more interesting approach is that of adding polymer waste into the FCC process, under suitable process conditions with the use of zero value of spent FCC catalysts, a large number of waste plastics can be economically converted into valuable hydrocarbons. The objective of this work is to explore the capabilities of a catalytic fluidised bed reaction system using spent FCC commercial catalysts for the study of product distribution and selectivity on the catalytic degradation of a post-consumer polyolefin waste (PP/PE mixture), and specifically for identification of suitable reaction conditions for enhancing the potential benefits of catalytic polymer recycling.

2. Experimental

2.1. Materials and experimental procedures

The catalysts employed are described in Table 1. All the catalysts were pelleted, crushed and sieved to give particle sizes ranging from 75 to 180 μm. The catalyst (0.25–0.3 g) was then dried by heating in flowing nitrogen (50 ml min^{-1}) to 120 °C at 60 °C h^{-1}. After 2 h the temperature was increased to 520 °C at a rate of 120 °C h^{-1} to active the catalyst for 5 h. In the case of the spent FCC catalyst, it could contain a certain amount of coke, and air was swept and maintained for 3 h at 600 °C to burn it off before activating. The polymer mixture used in this study was obtained from post-consumer plastic waste stream in South-Taiwan with the component of polyethylene (~67 wt% PE = ~40 wt% HDPE + ~27 wt% LDPE), polypropylene (~33 wt% PP). High purity nitrogen was used as the fluidising gas and the flow was controlled by a needle valve and preheated in the bottom section of the reactor tube. Flowmeters were used to measure the full range of gas velocities from the incipient to fast fluidisation. Before catalytic pyrolysis experiments were started, several fluidisation runs were performed at ambient temperature and pressure to select: (i) suitable particle sizes (both catalyst and polymer waste) and (ii) optimise the fluidising gas flow rates to be used in the reaction. The particle size of both catalyst (75–180 μm) and polymer (75–250 μm) were chosen to be large enough to avoid entrainment but not too large as to be inadequately fluidised. High flow rates of fluidising stream improve catalyst–polymer mixing and external heat transfer between the hot bed and the cold catalyst. On the other hand, an excessive flow rate could cause imperfect fluidisation and considerable entrainment of fines.

2.2. Experimental procedures and product analysis

A process flow diagram of the experimental system is given elsewhere [15] and shown schematically in Fig. 1. A three-zone heating furnace with digital controllers was used and the temperatures of the furnace in its upper, middle and bottom zones were measured using three thermocouples. By these means the temperature of the pre-heated nitrogen below the distributor and catalyst particles in the reaction volume could be effectively controlled to within ±1 °C. The polymer feed system was designed to avoid plugging the inlet tube with melted polymer and to eliminate air in the feeder. The feed system was connected to a nitrogen supply to evacuate polymer into the fluidised catalyst bed. Thus, commingled polyethylene/polypropylene (PE/PP) polymer particles were purged under

Table 1
Catalysts used in the catalytic degradation of post-consumer PE/PP polymer waste

Catalyst	Si/Al	Surfacea area (cm^2/g)			Pore size (nm)	Acidity[a] (μmol Py/g catalyst)		Commercial name
		BET[b]	Micro	External		Brφnsted	Lewis	
RCat-c1	2.1	147	103	44	–[c]	4.8	3.7	Equilibuium catalysts[d]
ZSM-5	17.5	426	263	128	0.55 × 0.51	33.4	19.8	ZSM-5 zeolite[e]
HUSY	13.6	547	429	118	0.74	33.4	19.8	Ultrastabilised Y zeolite[d]
SAHA	3.6	268	21	247	3.28[f]	0.1	22.6	Amorphous silica alumina[d]
Silicalite	>1000	362	297	65	0.55 × 0.51	–[g]		Synthesized in-house

[a] Measured by IR spectroscopy and adsorption–desorption of pyridine (Py) at 623 K for the amount of adsorbed Py (μmol/g) on both acid sites of catalysts.

[b] Total surface area (BET).

[c] The catalyst was a mixture of zeolite, a silica–alumina matrix and binder, not determined.

[d] Chinese Petroleum Corp., CPC, Taiwan, ROC.

[e] BP Chemicals, Sunbury-on-Thames, UK.

[f] Single-point BET determined.

[g] The sodium form of siliceous ZSM-5 with very few or no catalytically active sites, not determined.

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