



# Role of pore structure in the deactivation of zeolites (HZSM-5, H $\beta$ and HY) by coke in the pyrolysis of polyethylene in a conical spouted bed reactor

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## ABSTRACT

The deactivation of three different catalysts used in the cracking of high density polyethylene (HDPE) has been compared. The catalysts used are HZSM-5, H $\beta$  and HY zeolites agglomerated with bentonite and alumina. The reactions have been carried out in a conical spouted bed reactor at 500 °C, and plastic (high density polyethylene) has been fed in continuous mode (1 g min<sup>-1</sup>) for up to 15 h of reaction. The HZSM-5 zeolite catalyst gives way to high yields of C<sub>2</sub>–C<sub>4</sub> olefins (57 wt%) and, moreover, it is the one least influenced by deactivation throughout the run, which is explained by the lower deterioration of its physical properties and acidity. The results of temperature program combustion and transmission electron microscopy show that coke growth is hindered in the HZSM-5 zeolite pore structure. The high N<sub>2</sub> flow rate used in the conical spouted bed reactor enhances coke precursor circulation towards the outside of the zeolite crystal channels.

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## 1. Introduction

The increase in the production of plastics is due to a higher standard of living and to their availability at a relatively low cost. Nevertheless, this increase in the production of materials with progressively shorter periods of use and which are not biodegradable generates serious environmental problems. Amongst the solutions to avoid disposal or land filling are source reduction, reuse, recycling, recovery of the inherent energy value through waste-to-energy incineration, recovery of monomers, and fuel production [1].

Waste plastic pyrolysis (or thermal cracking) is the route of greatest interest for large-scale implementation in order to recover monomers, liquid fuel, hydrogen or synthesis raw materials [2–4]. Pyrolysis is especially suitable for treating polyolefins (high and low density polyethylene and polypropylene), which account for two-thirds of the plastics in municipal solid waste, and it may also be applied to other polymeric materials [5–7], their blends [8–11] and mixtures with other residues, such as biomass [12,13].

The technological development of waste plastic pyrolysis faces difficulties related to the endothermic nature of the reaction (heat

transfer method and rate are essential) and to the complex reaction mechanism. Consequently, product selectivity depends on raw material composition and reaction conditions (mainly temperature and volatile residence time in the reactor). The fluidized bed reactor, which generally contains sand as a fluidizing agent, has suitable features for plastic pyrolysis, such as high capacity for heat and mass transfer between phases and isothermicity. Accordingly, it has been used by several authors in discontinuous mode [14–17] and with continuous plastic feed [18].

Polyolefin cracking on acid zeolites takes place through carbocationic intermediates activated by Lewis and Brønsted sites, which has advantages over the mechanism with radical intermediates characteristic to thermal pyrolysis. These advantages are: (i) lower temperature and, consequently, energy saving; (ii) shorter residence time of the plastic, enabling higher production for the same reactor volume; (iii) higher selectivity of commercially interesting products. The catalysts commonly used are pure zeolites (HZSM-5, H $\beta$ , HY, HMCM-41) or those previously used in a fluidized bed in fluid catalytic cracking (FCC) units [19–21].

The main difficulty regarding plastic pyrolysis in continuous mode is the agglomeration of plastic particles that fuse when they are fed into the reactor. This problem causes defluidization of the bed due to the agglomeration of sand and/or catalyst particles coated with fused plastic. To avoid this problem, other types of reactors have been suggested, such as sphere circulation [22], particle stirring [23] and screw kiln [24,25]; all of which involve a mechanically forced movement of particles.

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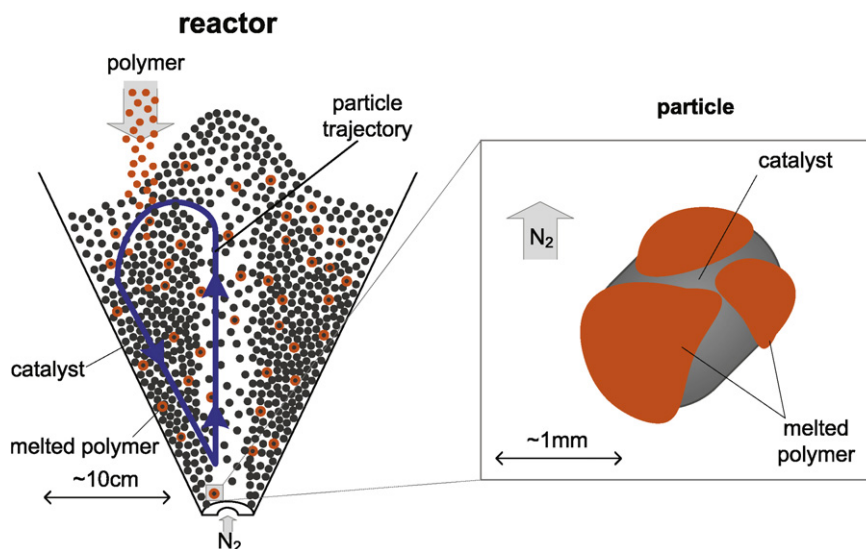


Fig. 1. Catalyst particles coated with fused plastic and their movement in the conical spouted bed reactor.

The catalytic transformation of plastic particles fed into a conical spouted bed reactor occurs through the stages of fusion, coating of catalyst particles, pyrolysis and catalytic transformation (Fig. 1).

The cyclic movement of particles in the conical spouted bed reactor enhances the uniform coating of particles with fused plastic. Moreover, owing to the high momentum transfer, the particles coated with plastic do not agglomerate when they collide into each other [26–28]. In addition, the high particle velocity in the spout breaks up any incipient agglomeration. This vigorous particle movement allows operating under conditions in which there is a high yield of waxes (primary products) at low temperatures and, consequently, energy requirements for the pyrolysis are minimal [29].

Given the high heat and mass transfer rate between phases, the restrictions on the physical steps are minimized and, consequently, the conical spouted bed reactor is appropriate for the kinetic study of plastic pyrolysis [30]. Furthermore, the short volatile residence time (hundredths of second) [31], gives way to high yields of monomers in polystyrene pyrolysis [32] and polymethyl methacrylate pyrolysis [33], with low yields of undesired secondary products, such as polyaromatics (PAHs).

Furthermore, cyclic particle movement avoids bed segregation [34,35], which is important for operation in continuous mode, given that catalyst particles coated with fused plastic have a wide size distribution. This feature is essential for the *in situ* use of the catalyst without segregation problems.

Previous studies [36,37] have shown that the conical spouted bed reactor performs well in the pyrolysis of polyolefins using *in situ* acid catalysts. Given that knowledge of catalyst deactivation by coke deposition is essential, this paper compares the deactivation of catalysts prepared with zeolites of different shape selectivity (HZSM-5, H $\beta$  and HY) used in the continuous pyrolysis of high density polyethylene (HDPE). Shape selectivity is a key factor for coke formation and, therefore, for the deterioration of the catalysts' physical properties and acidity in acid catalyst reactions [38,39].

## 2. Experimental

### 2.1. Pyrolysis equipment, conditions and product analysis

The equipment used for pyrolysis has already been described elsewhere [37]. The feeding system is pneumatically actuated and doses of plastic chips (with an average particle diameter of 4 mm)

are pulse fed through a 3-way hollow ball valve from a 2 L hopper. The amount of plastic that can be fed is limited by the reaction rate and the plastic flow rate for a 30 g catalyst bed is in the 0.5–2 g min<sup>-1</sup> range, with a feeding frequency ranging from 4 to 16 batches min<sup>-1</sup>.

The experimental conditions for the reactions are: 500 °C; 1 g min<sup>-1</sup> of HDPE; 30 g of catalyst bed; 12 L min<sup>-1</sup> of N<sub>2</sub> (measured at room conditions); time on stream, up to 15 h; catalyst particle size, between 0.6 and 1.2 mm.

High density polyethylene (HDPE) provided by Dow Chemical (Tarragona, Spain) with the following properties has been used: average molecular weight, 46,200 g mol<sup>-1</sup>; polydispersity, 2.89; density, 940 kg m<sup>-3</sup>; higher heating value, 43 MJ kg<sup>-1</sup>.

The reactor, with a volume of 3 L, has a conical shape (28° angle), with a cylindrical section at the upper part for fountain development. The total height of the reactor is 0.34 m, with a conical section of 0.20 m and a base of 0.02 m in diameter. The spout is generated by an opening at the base measuring 0.01 m in diameter. Two thermocouples are located inside the reactor (in the annulus of the bed and next to the wall). Total and differential pressure gauges are used to detect gas filter plugging.

The volatile outlet stream passes through a condensation system consisting of a stainless-steel condenser (where less than 50% of volatiles are collected) and two coalescence filters (made of epoxy-ester) in-line, which retain above 99.5% of aerosol particles larger than 0.1  $\mu$ m. The condensed liquid analysis has been carried out by means of a gas chromatograph connected to a mass spectrometer (Shimadzu QP2010S). Product identification has been improved by a GC  $\times$  GC-MS (Agilent 7890-Agilent 5975 inert XL MSD). The online analysis of the outlet stream has been carried out by using an Agilent 6890 gas chromatograph. The columns and conditions used for the analyses have been described in detail elsewhere [37].

### 2.2. Catalysts

Three catalysts prepared with zeolites HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30), H $\beta$  (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 75) and HY (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 5.2) supplied by Zeolyst international have been studied. The HZSM-5 zeolite has been supplied in the ammonium form, so it has been calcined at 550 °C to obtain the acid form. In order to obtain particles with a suitable size for the conical spouted bed reactor in the 0.6–1.2 mm diameter range, the zeolite particles (25 wt%)

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