



Effect of the acidity of the HZSM-5 zeolite catalyst on the cracking of high density polyethylene in a conical spouted bed reactor

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ABSTRACT

The catalytic cracking of high density polyethylene (HDPE) has been carried out at 500 °C in a conical spouted bed reactor with two catalysts prepared with HZSM-5 zeolites with SiO₂/Al₂O₃ ratios of 30 and 80. The polyethylene has been fed continuously (1 g min⁻¹) over 10 h to a 30 g catalyst bed. The results show the good performance of the conical spouted bed reactor in minimising the limitations of the physical steps of the process. The deactivation of the catalysts is very low and it is demonstrated that the moderation of the acidity is useful in modifying the product distribution. The SiO₂/Al₂O₃ ratio increment involves a decrease in the total acidity and in the acid strength, resulting in a higher yield of C₂–C₄ olefins and that of the non-aromatic C₅–C₁₁ fraction, and a decrease in the yields of aromatic components and C₁–C₄ paraffins. The yield of the C₂–C₄ olefins obtained with the HZSM-5 zeolite catalyst with a ratio of Si/Al₂O₃ = 80 is 59.8 wt% (that of propylene is 29.6 wt%) and the yield of the gasoline fraction (C₅–C₁₁) accounts for 32.1 wt%. The coke deposited on the catalyst has a heterogeneous nature and is constituted by two types of coke, which are deposited on the exterior and the interior of the crystalline channels of the HZSM-5 zeolite. The evolution of the coke is attenuated as the SiO₂/Al₂O₃ ratio of the zeolite is increased.

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1. Introduction

The waste plastic recycling via pyrolysis is a matter of high interest in obtaining fuels and for monomer recovery [1–3]. However, the industrial application of the pyrolysis processes requires a solution for problems such as: (i) the energetic requirements, due to the endothermic nature of the pyrolysis and the low thermal conductivity of the plastics; (ii) the difficulty of the plastic management, which melts prior to pyrolysis, transforming into a very sticky material; (iii) the heterogeneity of the products.

Among the different reactors studied in the literature for plastic pyrolysis, the fluidised bed reactor performs well in terms of heat and mass transfer and it also has an acceptable performance for the coating of the sand or catalyst with melted plastic [4,5]. It has been demonstrated that the conical spouted bed reactor has especially good properties for avoiding the aforementioned problems, which allows for working in a continuous regime with higher plastic flows by reactor volume unit and with a higher versatility than in a fluidised bed reactor [6]. The cyclic movement of the sand or catalytic particles in the conical spouted bed facilitates the homogeneous coating of the particles with melted plastic and

even more, minimises defluidisation, preventing the agglomeration of particles when they collide [7]. Moreover, the low residence time of the pyrolysis products limits the secondary reactions of overcracking and condensation, which is important for minimising the formation of methane and polyaromatics (PAH), respectively [6,8,9].

On the other hand, due to the reduced segregation, the conical spouted bed reactor proves adequate for catalytic cracking in continuous regime, using acid catalysts in situ [10,11]. In the literature, catalysts prepared based on different zeolites (HY, HZSM-5, H β , MCM-41 among others) have been studied using different reactors [11–19], with the goal of decreasing the required temperature for pyrolysis and adapting the composition of the products to obtain raw materials of commercial interest (monomers or BTX aromatics) or transportation fuels. The apparent activation energy for the catalytic cracking of HDPE with modified HZSM-5 and HY zeolites falls in the range of 60–110 kJ mol⁻¹ measured by means of TG/DSC analysis, with the lowest values being for those zeolites with the highest acidity. These activation energies are lower than those obtained by the same authors in the thermal cracking (111 kJ mol⁻¹) [20,21]. Coelho et al. [22] have determined that the temperature required for HDPE cracking falls by 75 °C (down to 400 °C) using an HZSM-5 zeolite with a considerable acidity, with the product stream having a high content of the C₃–C₄ fraction, which increases along with the acidity, whereas the yield of the C₆–C₇ fraction decreases.

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