

HZSM-5 CATALYST DEACTIVATION IN THE CRACKING OF POLYOLEFINS IN A CONICAL SPOUTED BED REACTOR

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Abstract

In the pyrolysis-cracking of polyolefins, the catalyst suffers deactivation by coke. We have studied the deactivation of a HZSM-5 catalyst in terms of activity decay, deterioration of the catalytic properties and coke composition. The reactions were performed in a conical spouted bed reactor by continuously feeding the solid plastic –high density polyethylene (HDPE) and polypropylene (PP)– for 30 h, atmospheric pressure and 500 °C. Samples of the spent catalyst were collected from the reactor at different times-on-stream and then analysed using TG-TPO, N₂ and NH₃ adsorption, Raman, FTIR, UV-vis, ¹³C NMR spectroscopies, and submicron imaging: TEM, polarized-light-, FTIR- and Raman-microscopies). Combining the kinetic results with the deterioration of the catalyst and the properties of coke, we have explained the formation and the character of the coke.

Keywords: catalyst deactivation, coke; MFI, BEA, FAU zeolite; pyrolysis, cracking, plastics

1. Introduction

The pyrolysis of plastics, particularly of polyolefins, is an interesting pathway for obtaining fuels or recovering the original monomers [1,2]. Using an acid catalyst in the pyrolysis reactor leads to more efficient operation, and enhanced selectivity toward the formation of C₂-C₄ olefins when an HZSM-5 zeolite is used, or gasoline when a HY zeolite is used [3]. The conical spouted bed reactor has a cyclic movement of the particles, which improves the melting of the plastic, and the homogeneous coating of the catalyst. Thus, the physical steps do not have a role on the product yields and selectivities.

The main obstacle for the scale-up of the cracking of plastics is the deactivation of the catalyst caused by coke deposition [4]. In this work we have studied the deactivation of acid catalysts used for the pyrolysis of HDPE and PP in terms of activity decay, degradation of the catalytic properties and coke composition.

2. Materials and Methods

The catalyst was prepared through wet extrusion agglomerating 25 wt% of zeolite (HZSM-5 with SiO₂/Al₂O₃= 30, Zeolyst International), bentonite (Exaloid, 30 wt%) and α-Al₂O₃ (Martinswerk, 45 wt%). The agglomeration is intended for giving extra resistance against attrition in the fluidized bed, and for increasing the volume of macro and mesopores of the catalyst. The particles were obtained after wet extrusion, drying (120 °C, 24 h), crushing-sieving (0.6-1.2 mm), and calcination (550 °C, 3 h). The reactor is a conical spouted bed of 3 L capacity. Conditions: 500 °C, 1 bar. The bed consists of 30 g of catalyst, and plastic (HDPE or PP) was

continuously fed (1 g min⁻¹) through the top of the reactor, up to 1.6 kg [3]. Samples of the deactivated catalyst were taken at different values of time-on-stream. The analyses of hydrocarbon products were conducted with on-line and off-line chromatographs.

The methods used for characterizing the catalyst and the coke were: TG-TPO, N₂ and NH₃ adsorption, Raman, FTIR, UV-vis, ¹³C NMR spectroscopies, and submicron imaging: TEM, polarized-light-, FTIR- and Raman-microscopies.

3. Results and Discussion

Figure 1 shows the evolution of product yields with time-on-stream (which is proportional to the amount of plastic fed into the reactor) during the pyrolysis of PP. The products can be lumped into waxes (C₁₂₊), light olefins (C₂₋₄), light paraffins (C₂₋₄), PONs (paraffins, olefins and naphthenes) C₅₋₁₁, aromatics C₅₋₁₁, and coke. As observed in Figure 1, the yield of waxes increases over time-on stream (at the expense of the decrease in light paraffins, and aromatics). This result is linked to the catalyst deactivation. The yield of olefins peaks (at weight of plastic of 800 g) due to the fact that olefins are intermediates from the cracking of waxes and paraffins, in the formation of aromatics and coke.

Figure 2 shows the degradation of the physical properties of the catalyst, surface area (S_{BET}), and surface of micropores (S_{micropore}), upon a pyrolysis run of HDPE (similar deactivation as Figure 1). The deterioration of the properties has an initial fast evolution (weigh of plastic < 200 g, time-on-stream < 200 min) and reaches steady deactivation. This result is consistent with the evolution with time-on-stream of the yield of wax observed in

Figure 1. Furthermore, the number of active sites (acidity of the catalyst, which is not shown here) is also reduced in identical manner as the surface area.

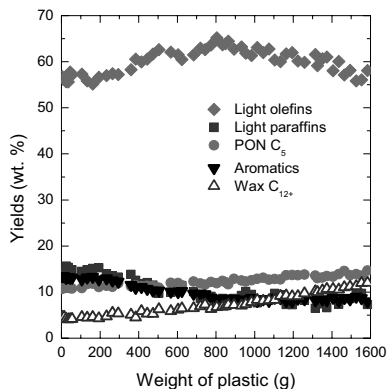


Figure 1. Evolution of the yields of different lumps with the amount of PP fed into the reactor.

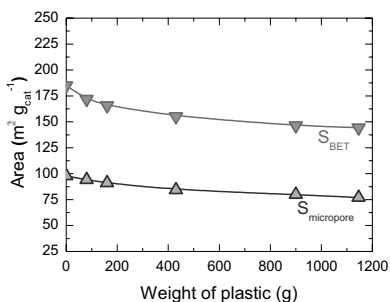


Figure 2. Evolution of the surface area (S_{BET}) and micropore area ($S_{micropore}$) during the pyrolysis of HDPE.

The content of coke have been measured using thermo-gravimetric analysis of coke combustion. The use of temperature programmed oxidation (TPO) ramp show two peaks of combustion, as it is shown in the sub-graph of Figure 3. This result led us to deconvolute the profile of combustion into two peaks: (1) type I coke, with the combustion peak at ca. 450 °C; and (2) type II coke, with the combustion peak at ca. 550 °C. Together with the results of Raman, FTIR and UV-vis spectroscopies, we have assigned type I coke to aromatic species with many aliphatic chains, external to the micropores of the zeolite; type II coke is made up of mainly aromatic structures deposited inside the micropores of the zeolite, and it is the main cause responsible for the deactivation. Figure 3 shows that there is a very fast initial formation of type II coke and then a steady increase, together with type I coke.

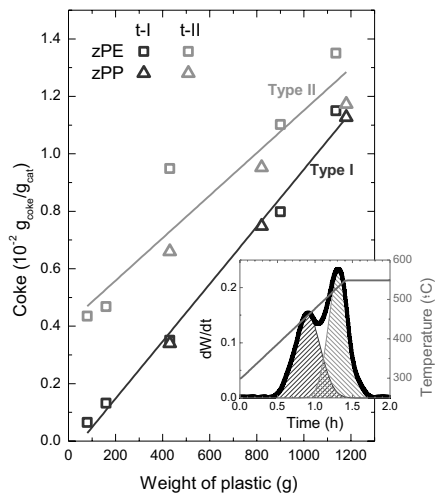


Figure 3. Evolution of the coke-species with the amount of plastic (both HDPE and PP) fed into the reactor.

4. Conclusions

The conical spouted bed reactor together with HZSM-5 catalyst are suitable for the catalytic pyrolysis of polyolefins, giving way to high yields of olefins and low amounts of aromatic components in the liquid product fraction. The operation in continuous mode is only affected by the catalyst deactivation. It is noteworthy that the partially deactivated HZSM-5 catalyst maintains its activity almost constant, with a slight change in product distribution due to coke deposition. Coke can be divided into type I coke (of aromatic-aliphatic nature) on the mesopores of the catalyst; and type II coke (of aromatic nature) inside the micropores of the catalyst, which is main cause responsible for the degradation of the properties of the catalyst and the deactivation.

References

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