Polymer Degradation and Stability 124 (2016) 51–59

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

# Mechanism and kinetics in catalytic hydrocracking of polystyrene in solution

Edwin G. Fuentes-Ordóñez, Joseba A. Salbidegoitia, María P. González-Marcos*, Juan R. González-Velasco

*Group of Chemical Technologies for Environmental Sustainability, Department of Chemical Engineering, Faculty of Science and Technology, The University of the Basque Country, UPV/EHU, P.O. Box 644, E-48080 Bilbao, Spain*

ARTICLE INFO

*Article history:*
Received 27 July 2015
Received in revised form
1 December 2015
Accepted 16 December 2015
Available online 19 December 2015

*Keywords:*
Polystyrene
Hydrocracking
Catalyst
Mechanism
Kinetics

ABSTRACT

A mechanism for polystyrene hydrocracking on a bifunctional Pt/H-Beta catalyst has been proposed. The mechanism consists of three steps for polymer degradation: initiation, propagation and termination, and an additional step for transformation of aromatics, direct product of polystyrene degradation, into other hydrocarbons. The most important reactions in the last step are hydrogenation–dehydrogenation and ring opening reactions, to produce naphthenics, paraffins and isoparaffins, with higher added value as fuels. Finally, degradation of polystyrene by catalytic hydrocracking has been described by means of continuous distribution kinetics, which allows for modelling of the evolution of polymer molecular size and conversion with reaction time, and estimation of kinetic parameters associated to catalyst characteristics when working in the kinetic regime.

## 1. Introduction

In recent years, plastic wastes energetic valorization processes have been focused on the production of hydrocarbons with high added value and easy commercialization, such as fuels [1–7]. Strategies under study at present, such as cracking, hydrocracking or hydroreforming, are based on emulation of petrochemical processes which, through the use of catalysts, direct macromolecule conversion mechanisms towards a wide variety of products [8–12].

Catalysts based on zeolites have been those most intensely studied and most promising for different energetic valorization processes, as they present certain characteristics which can be tailored for their application to plastic wastes [13–19]. One of the advantages of this approach is that it can be applied to plastic mixtures, which prevents expensive separation processes, and the product quality would be related to the chemical composition of the plastic waste mixture [20–23].

Polyethylene is known to produce mostly *n*-paraffins and 1-olefins, both in thermal and catalytic degradation processes [24–26]. Something similar occurs with polypropylene, where the trend upon degradation is to produce $C_5$–$C_{11}$ hydrocarbons of paraffinic, olefinic and aromatic nature [24,27–30]. Polystyrene, on the contrary, presents a high selectivity to the production of aromatic hydrocarbons, whose concentration is restricted in fuels [31–33].

Among the different processes focused on fuel production –pyrolysis, catalytic cracking and hydrocracking-, the latter presents several advantages concerning product quality, as it unifies in a single step cracking and hydrotreatment processes. In this way, the process would allow for saturation of olefins, transformation of paraffins into isoparaffins, and promotion of ring opening and aromatic hydrogenation reactions. All these reactions are crucial from the point of view of fuel production [3,10,34,35].

In a previous paper, the operation conditions for working in the kinetic regime in plastic hydrocracking were optimized, as gas–liquid and liquid–solid mass transfer resistances were minimized [36].

This work is focused on the reaction mechanism and kinetics of plastic hydrocracking. The aim of the work is to determine the possible simultaneous pathways involved in degradation and transformation of polystyrene into valuable hydrocarbons such as fuels. Moreover, a kinetic model of polystyrene hydrocracking is proposed, based on continuous distribution kinetics, which allows for description of the molar and weight change along the reaction.

---

* Corresponding author.
*E-mail address:* mp.gonzalezmarcos@ehu.es (M.P. González-Marcos).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.12.009

This model, applied under kinetic control, could be used to compare catalyst activity for the process.

## 2. Experimental

### 2.1. Catalysts preparation

H-Beta in powder form (Zeolyst Corp., $SiO_2$:$Al_2O_3$ ratio of 25, calcined at 773 K for 2 h) was used as catalytic support. Platinum was incorporated to the support by ionic exchange from solution. 10 g of the support were slurred in deionised water (1 L) and then heated to 353 K under continuous stirring. Then, a 0.01 M solution of $[Pt(NH_3)_4](NO_3)_2$ (Alfa Aesar, 99.99%) was slowly added to the mixture and the pH adjusted to 7 with either $NH_3$ or $NH_4NO_3$. The mixture was kept at 353 K under stirring for 24 h, at pH 7 [37–39]. The mixture was then filtered and washed with deionised water for three times, and the precursor dried overnight at 393 K. After that, the precursor was calcined (0.5 K $min^{-1}$ up to 723 K, and 2 h at 723 K), and finally reduced in a flow of $H_2$ (60 $cm^3$ $min^{-1}$) while the temperature was raised from room temperature up to 723 K at a rate of 3 K $min^{-1}$ and then kept at that temperature for 2 h.

### 2.2. Characterization of catalysts

Surface area, external surface, and pore size distribution in the micropore and mesopore range were determined by $N_2$ physisorption at 77 K, using the conventional BET, t-plot, Horvath–Kawazoe and BJH methods, in a Micromeritics ASAP 2010 instrument. The sample was degassed (<1.5 Pa) at 573 K for 12 h and, afterwards, the isotherm was obtained.

Acidity was evaluated by temperature programmed desorption (TPD) of ammonia in a Micromeritics Autochem 2910, equipped with TCD. The sample was reduced in 50 $cm^3$ $min^{-1}$ of 5% $H_2$/Ar with a heating rate of 10 K $min^{-1}$ from room temperature up to 723 K, where the temperature was kept for 1 h. After that, the flow was changed to He and the temperature was kept at 723 K for one additional hour. Then, the sample was cooled to 373 K. Adsorption of $NH_3$ was performed by successive pulses of 0.25 $cm^3$ of 10% $NH_3$/He, until saturation of the catalyst sample. Finally, physisorbed $NH_3$ was removed by a 2 h treatment in 50 $cm^3$ $min^{-1}$ He. TPD was carried out with a heating rate of 10 K $min^{-1}$ from 373 to 723 K.

Actual metallic loading was determined by inductively coupled plasma (ICP), using a Varian (710-ES ICP-Optical in radial position) equipment. An adequate amount of catalyst sample, in order to obtain metal concentration in the linear range of measurement, at 214.424 nm, was dissolved in aqua regia and hydrofluoric acid, and heated until complete evaporation of the liquid. Then, the remaining solid was dissolved in an aqueous solution with 2% nitric acid.

Metallic dispersion was evaluated by $H_2$ chemisorption in a Micromeritics ASAP 2020C instrument, at 308 K. Firstly, the sample was degassed (<1.5 Pa) for 12 h at 573 K, and then reduced in $H_2$ flow at 623 K during 2 h. Afterwards, hydrogen was removed by a vacuum treatment (<1.5 Pa) at 633 K for 1.5 h and then the sample was cooled down to 308 K. Two successive isotherms were carried out, with intermediate evacuation (<1.5 Pa, 308 K, 30 min), and subtraction of the latter to the former allowed for evaluation of the irreversibly chemisorbed hydrogen.

### 2.3. Polystyrene hydrocracking system and analysis

Fig. 1 shows a schematic diagram of the experimental system used for hydrocracking. The reactor (Autoclave Engineers, Hastelloy C-276), with a capacity of 300 mL, is equipped with: a high speed rotary stirrer operated by a magnetic system; temperature, pressure, inlet and outlet flow controllers; inlet and outlet pipes; and a reflux condenser.

Virgin PS with different molecular weight (35,000 and 192,000 g $mol^{-1}$) was provided by Aldrich. Before reaction, PS was milled to an average particle size of 1 mm in a mill (Retsh ZM 200) refrigerated with liquid nitrogen.

The reactions were performed with PS either pure or solved in decahydronaphthalene (DHN; mixture 34%*cis*-66%*trans*, Sigma–Aldrich) and catalyst in a slurry (Pt/H-Beta, average particle size 230 μm). The reaction mixture was introduced in the reactor, which was then closed and heated to operation temperature. At this point (t = 0), the system was pressurized under $H_2$ and stirring was started. The system was run for a specific time, and samples for analysis were taken at specific intervals. Finally, stirring was stopped and the reactor was allowed to cool down to room temperature.

The degree of conversion of PS was evaluated by gel permeation chromatography (GPC, Waters 616) in line with Ultraviolet (Acquity) and Refraction Index (Waters 2410) detectors, by following PS molecular weight distribution and concentration in solution, after calibration. The GPC was equipped with Styragel HR1 and HR4 columns placed in series in an oven set at 308 K, in order to cover the molecular weight range of 100–500,000 g $mol^{-1}$. THF (1 mL $min^{-1}$) fed by a Waters 515 HPLC pump was used as mobile phase.

## 3. Results and discussion

### 3.1. Catalyst

The main characteristics of the Pt/H-Beta catalyst used in this study are summarized in Table 1. From the point of view of the present study, the most interesting aspects are its bifunctionality, with both metallic and acidic sites, and the important contribution of the mesoporosity to the surface area, with a wide distribution of diameter sizes in the 2–80 nm range, as shown in Fig. 2, that favours the access of the big reactant molecules to the active sites.

### 3.2. Reaction mechanism

PS degradation during hydrocracking was followed by GPC. Fig. 3 shows the evolution of the reaction products with time. We can see that molecular weight of polystyrene decreases with reaction time, which indicates a random scission of polymeric chains. Moreover, the intensity of the peak corresponding to polymer also decreases with reaction time, while the intensity of peaks associated to trimers, dimers and monomers or transformed monomers increases.

When the evolution of GPC with time in Fig. 3 is compared to the data found in the literature for thermal [40] and catalytic [41,42] degradation of PS, a reaction mechanism can be inferred with the classical initiation, propagation and termination steps.

Although hydrocracking is a catalytic process, thermal reactions are also involved in polymer degradation. Regarding catalytic reactions, the complexity of the bifunctional catalyst, with acidic (Lewis and Brønsted) and metallic active sites, must be considered.

#### 3.2.1. Initiation

In this step, the polymeric chain is broken into two shorter chains. Fig. 4 shows the evolution of PS molecular weight distribution during hydrocracking, which can be considered an indicative of the initiation step.

Chain scission reaction mechanisms of low molecular weight hydrocarbons, based in the chemistry of carbenium ion [43], have been proposed to be used for extrapolation to polymer chain