

POLYSTYRENE HYDROCRACKING IN SOLUTION OVER BIFUNCTIONAL CATALYSTS

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Abstract

Polystyrene hydrocracking in solution was successfully studied in batch reactor at 648-685 K, under H₂ at 3-6 MPa, 1200 rpm, 0-50 wt.% of PS, 0-240 min, over bifunctional catalysts and in the absence of catalyst. Comparing thermal and catalytic processes, different reaction mechanisms can be observed to be involved in PS degradation depending on type of acidic sites. Metallic and Lewis sites promote hydrogenation-dehydrogenation reactions which initiate the degradation, followed by β -scission to become radicals and end-chain β -scission to produce low molecular weight hydrocarbons; unfortunately they also terminate PS degradation by radical hydrogenation. Over Brønsted centres, a phenyl group is attacked and released to produce benzene and radicals that propagate with end-chain β -scission. Metallic and Brønsted sites also promote ring opening reactions which decrease aromatic content in final product. With respect to operation conditions, high H₂ pressure and temperature contribute both to PS degradation and ring opening reactions.

Keywords: polystyrene, hydrocracking, catalyst, Brønsted, Lewis, platinum

1. Introduction

Nowadays, polymer degradation is being studied in terms of environmental solution to waste plastics and recovery of such an energetic source. Many studied processes, such a pyrolysis, catalytic and thermal cracking [1], could have applications in recovery of monomer. However, obtaining fuels needs ulterior hydro-conversion to reduce aromatic fraction in the products [2]. The aim of this study is to obtain a fraction of fuels with high quality through hydrocracking.

2. Materials and Methods

Hydrocracking reactions were performed with 30 wt.% PS in decalin and 0.3% of catalyst. The reactor was heated at 648-685 K for 60 to 240 min, under H₂ at 6 MPa and 1200 rpm. Gas and liquid products were analyzed by GC-FID and GPC-IR. In Table 1, some characteristics of the catalyst used are presented.

3. Results and Discussion

Time on stream: High rate of PS degradation is observed at low reaction times for both thermal and catalytic

reactions. PS conversion above 50 % is reached in the first 60 min. Imperfections in original PS chains are thought to be responsible for initial conversions.

Pressure: Increasing H₂ pressure slightly favors PS degradation; moreover, high pressures promote ring opening reactions and reduce catalyst deactivation.

Temperature: High temperature has a positive effect in conversion of PS, additionally encouraging ring opening and cracking reactions. However, undesired dehydrogenation reactions are also favored by increasing temperature.

Catalyst: Figure 1 shows PS and decalin conversion, and distribution of products for both thermal and catalytic process. Catalysts with high acidity and low Brønsted:Lewis ratio, Pt/Al₂O₃ and Pt/H-Y, are observed to produce lower PS conversion than thermal process. On the other hand, Pt/H-Bea, that present less acidity but the highest B/L ratio, reaches complete conversion of

Table 1. Catalyst characterization

Catalyst	S _{BET} (m ² ·g ⁻¹)	Pt (% wt)	Acidity (μmolNH ₃ ·g ⁻¹)			B/L
			Total	Weak	Strong	
Pt/Al ₂ O ₃	221	0.3	550	180	370	-
Pt/H-Y	661	0.5	600	340	260	1.1
Pt/H-Bea	447	0.5	310	150	190	1.6

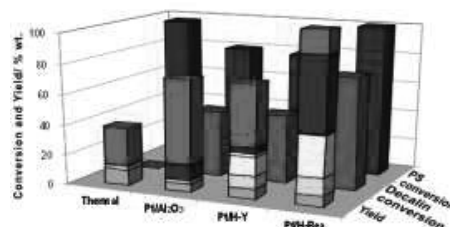


Figure 1. Conversion and product distribution of PS hydrocracking in solution at 673 K, 6 MPa H₂, 1200 rpm and 240 min. □ P □ I ■ A ■ N □ O ■ Oligomers.

PS. These results suggest that different reaction mechanisms are involved over each catalyst.

Polymer degradation is known to follow 3 steps: initiation, propagation and termination. Firstly, in the thermal process, initiation occurs mainly by breakage of C-C bonds to obtain radicals; then, in propagation, hydrogen transfer and β -scission reactions take place, to produce monomers, dimers and trimers; and recombination, radical addition and disproportionation are termination reactions [3]. Secondly, over Pt/Al₂O₃, which is a bifunctional catalyst with metallic and acidic Lewis centres, initiation is associated to C-H bond fission and β -scission; propagation occurs by alkyl and chain-end fission reactions and undesired termination reactions like radical hydrogenations. Finally, over Pt/H-Y and Pt/H-Bea, in addition to metallic and Lewis centers, there are acidic Brønsted centers, and other initiation reactions can be included, described as an attack to a proton on the phenyl group followed by releasing of benzene to produce a cation and β -scission to produce radicals [4].

With respect to decalin conversion, decalin is observed to be thermally stable but, in the presence of a catalyst, both metallic and acidic sites are responsible for conversion of decalin. However, we can clearly see that metallic and Lewis sites promote hydrogenation-dehydrogenation reactions, while metallic and Brønsted centers promote ring opening and cracking reactions. Ring opening reactions are widely desired because they contribute to reduce aromatic content in final products.

Through detail hydrocarbon analysis, the following lumps are used to present the product distributions: paraffins (P), isoparaffins (I), aromatics (A), naphthenes (N), olefins (O) and oligomers. The results shown in Figure 1, support the reaction mechanisms above mentioned. Firstly, oligomers and a highly aromatic fraction are obtained in the thermal process. Then, oligomers, aromatic products, from PS degradation and decalin dehydrogenation, and naphthenes, which are obtained by aromatic lump hydrogenation, occur over Pt/Al₂O₃. Finally, over Pt/H-Y and Pt/H-Bea, oligomers from PS degradation, aromatics from PS and decalin ring opening; naphthenes, as a product of hydrogenation of aromatics; olefins, paraffins and isoparaffins, as a product of ring opening and cracking reactions of decalin and naphthenes derived from PS, are produced.

PS concentration: Reactions with concentration up to 50 wt.% in PS were carried out over Pt/H-Bea. It is noteworthy that, in all cases, PS degradation was complete before 240 min.

Yield and product distribution by number of carbons and type of hydrocarbons are shown in Figure 2. C₁-C₃ hydrocarbons are observed to be paraffins formed by cracking reactions, and their yield increases with PS concentration. C₄-C₅ are isoparaffins and paraffins, probably produced by ring opening of single ring aromatic compounds. C₆-C₈ is an aromatic fraction that increases with PS initial concentration and naphthenes from hydrogenation reactions; benzene and cyclohexane

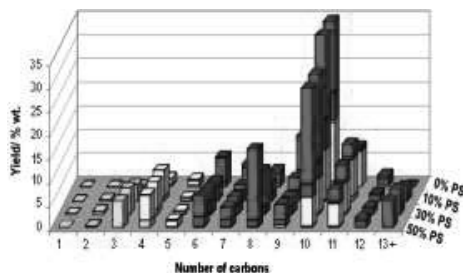


Figure 2. Product distribution of PS hydrocracking in solution over Pt/H-Bea at 673 K, 6 MPa H₂, 1200 rpm and 240 min reaction time.

in C₆ are probably obtained by PS degradation over Brønsted centers, whereas toluene, ethylbenzene and their hydrogenated products in C₇ and C₈ are formed over Lewis centers. In fraction C₉-C₁₂ there are aromatics, naphthenes and isoparaffins, mainly produced by decalin reaction. Finally, in C₁₃₊ there are aromatic compounds, which are associated with oligomers from PS degradation; this fraction increases with PS content.

4. Conclusions

Differences in PS conversion and product distribution can be explained by changes in the reaction mechanisms of PS degradation in the absence and in the presence of acidic catalysts. Acidic catalyst with high Brønsted:Lewis ratio are observed to be favorable to PS degradation and, moreover, this kind of catalysts produce a huge variety of products, because they promote further reactions such as hydrogenation-dehydrogenation, ring opening and cracking. This fact contributes to improve the quality of the product.

Increasing PS initial concentration does not have a huge impact in the reaction because, until 50 wt.% of PS, PS was observed to be successfully converted into C₁-C₈ hydrocarbons. The increase of initial viscosity may cause problems in mass and heat transfer, but the initial high reaction rates compensate this fact.

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