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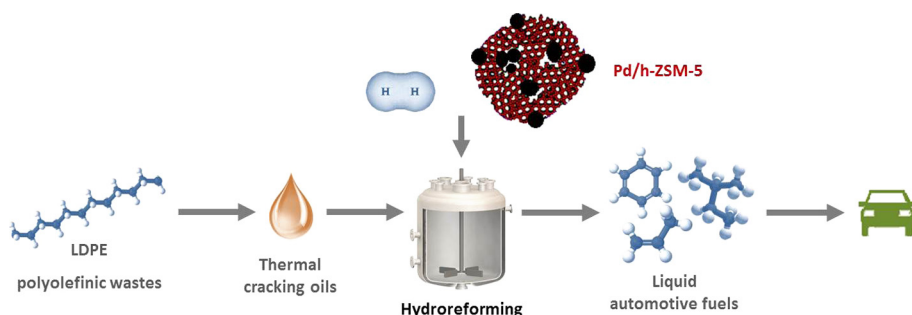
# Hydroprocessing of the LDPE thermal cracking oil into transportation fuels over Pd supported on hierarchical ZSM-5 catalyst

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## HIGHLIGHTS

- Hierarchical porosity in ZSM-5 zeolite leads to a high Pd dispersion.
- Hydroprocessing of LDPE thermal cracking oil is enhanced by zeolite mesoporosity.
- The raw oil is greatly upgraded aimed at the formulation of transportation fuels.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The oil obtained by LDPE thermal cracking, which is formed by linear olefins and paraffins with a broad carbon atom range, has been upgraded by hydroprocessing over Pd/ZSM-5 catalysts. As a consequence of this treatment, gasoline and diesel range hydrocarbons are produced with an enhanced content of isoparaffins and aromatics, while the presence of olefins is strongly reduced. The use of hierarchical zeolitic supports with a secondary porosity has a positive effect on the catalytic activity in the main reactions taking place (hydrogenation, hydroisomerization, cracking, oligomerization and aromatization), which is assigned to the higher reactant accessibility achieved with the hierarchical ZSM-5 compared to a nanocrystalline ZSM-5 sample used as reference. On the other hand, the acidic features of the zeolite have been controlled by variation of the Si/Al ratio in the 30–300 range, which has allowed adjusting the extension of the metal and acid sites catalyzed reactions.

In overall, the use of Pd/h-ZSM-5 catalysts allows the hydroprocessing of the LDPE thermal cracking oil to be conducted in an effective way improving significantly the feed properties regarding its potential use in the formulation of transportation fuels. Thus, adjusting the catalyst properties and the operating conditions it is possible to achieve a high selectivity towards liquid fuels (over 95%), avoiding excessive cracking, and to control their composition leading to high isoparaffins and aromatics content with a low share of olefinic compounds. Finally, a reaction scheme has been proposed taking into account the main transformations occurring during the hydroprocessing treatment.

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## 1. Introduction

Polyolefinic plastic wastes, consisting of polyethylenes and polypropylene, make up roughly 50% of the total share of the plastic waste streams [1]. This fact is particularly interesting since this

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class of plastic residues might be upgraded through their conversion into fuels and/or chemicals [1–3]. Fuel production from polyolefins can be attained by thermal decomposition. Thus, pyrolysis of polyethylenes leads to hydrocarbon mixtures within a broad carbon atom number interval (up to about  $C_{40}$ ), comprising mostly the n-paraffin and the 1-olefin corresponding to each carbon atom number [4–6]. These hydrocarbons mixtures cannot be used directly as transportation fuels, since they contain a high concentration of olefins that can form unwanted gums. Additionally, the presence of mostly linear hydrocarbons originates gasolines with low Octane Numbers and diesel fuels with high pour points.

Catalytic cracking of polyolefin plastics allows obtaining hydrocarbon mixtures in which the products distribution depends on the employed catalyst. In this regard, a variety of conventional zeolites [7–10], ordered mesoporous materials [11–13], FCC catalysts [14,15], as well as nanocrystalline and hierarchical zeolites [16–18], have been tested in the catalytic cracking of polyolefins. Hierarchical zeolites have resulted in enhanced activities due to the presence of mesopores that increase the accessibility of bulky macromolecules to the acid sites. However, the obtained hydrocarbon mixtures contained a great share of olefins, so they were still inadequate to be used as transportation fuels. Additionally, the direct contact of the catalyst with the plastic wastes makes difficult its further separation from the impurities present in the feed and favours the catalyst deactivation by poisoning [13,19].

In light of these facts, a two-stage process has been recently proposed to solve the aforementioned drawbacks, comprising a first thermal cracking treatment of the polyolefins followed by catalytic hydroprocessing of the obtained oils [6,19,20]. This process enables to remove the olefins as well as to tune the properties of the fuels by choosing suitable catalysts and operation conditions. Since the hydroprocessing reactions require active sites capable of capturing and dissociating hydrogen molecules, a metallic phase is usually supported on the acidic material. Thus, catalysts based on Ru and Ni supported over hierarchical Beta zeolite have been tested in the hydroreforming reaction of the polyethylene thermal cracking oil [21,22]. In the case of the Ru-containing catalyst, after a regeneration treatment, it showed worse properties in the second cycle of reaction due to both the formation of larger aggregates of Ru particles concentrated in certain areas of the catalyst and to Ru leaching [21]. On the other hand, Ni supported on hierarchical Beta zeolite has shown good properties for this reaction, leading to more than 80 wt% automotive fuels, mainly gasoline ( $C_5$ – $C_{12}$ , 54 wt%) with a high Research Octane Number. This performance was ascribed to the hierarchical nature of the employed Beta zeolite sample that provided a good dispersion of the metal phase as well as an enhanced accessibility of the reacting molecules towards the active sites through the mesopores [19]. However, the small size of the Ni particles supported over hierarchical Beta zeolite led towards lower selectivities to aromatics and isoparaffins, increasing somewhat the extent of the hydrocracking and hydrogenation reactions [22]. Ni supported on hierarchical ZSM-5 has been tested also in this process [19], although resulting in an enhanced gas production due to its stronger acidity compared to zeolite Beta. However, ZSM-5 exhibits the advantage of being easily prepared encompassing a wide range of Si/Al ratios.

In this context, the present work is aimed at investigating the behavior of catalysts based on Pd/ZSM-5 in the hydroreforming of the polyethylene thermal cracking oil. Pd has been widely reported as a very active metal in hydro/dehydrogenation and hydroisomerization reactions [23–25], requiring much lower amounts compared to Ni. On the other hand, regarding the zeolitic support, two main features are addressed in the current work. The first one is the presence of a hierarchical porosity in order to improve the dispersion of the Pd particles and the second one is the fine tuning of the zeolitic support acidity by varying its Si/Al

ratio. The results here reported show that adjusting the support acidity in the Pd/ZSM-5 system is a very effective way for decreasing the extent of unwanted cracking reactions, responsible for the abatement of the yields into liquid fuels, holding an adequate balance of hydroisomerization, aromatization and hydrogenation reactions. Moreover, the strong acidity of this zeolite, in combination with the presence of mesoporosity, enhances also the production of branched and aromatic compounds, giving rise to high quality gasoline and diesel fuels.

## 2. Experimental section

### 2.1. Synthesis and characterization of the Pd/h-MFI catalysts

Hierarchical h-ZSM-5 samples were synthesized according to a protozeolitic units silanization method described elsewhere [26]. The synthesis gels were prepared containing distilled water, tetraethoxysilane (TEOS, 98% Aldrich, as silica source), tetrapropylammonium hydroxide (TPAOH, 40% v/v aqueous solution, Alfa, as structure directing agent) and aluminum isopropoxide (AIP, Aldrich, as aluminum source) in varying proportions in order to have initial Si/Al molar ratios of 30, 50, 100 and 200. The gels were precrystallized at 90 °C for 20 h under reflux and then phenylaminopropyltrimethoxysilane (Aldrich), in proportion of 8 mol% related to the silica content, was added and left reacting for 6 h. The final solutions were crystallized in Teflon-lined autoclaves at 170 °C for 7 days. The solid products were separated by centrifugation, rinsed with distilled water, dried overnight at 110 °C and calcined in air at 550 °C for 5 h. The obtained materials were named as h-ZSM-5 (X), where X stands for the obtained Si/Al ratio. Additionally, for comparison purposes, a nanocrystalline ZSM-5 (Südchemie) was also used and denoted as n-ZSM-5.

Palladium was incorporated on the supports by impregnation with a  $PdCl_2$  (>99.9%, Aldrich) aqueous solution. The concentration of this solution was adjusted to get 1 wt% Pd in the final materials. Impregnated samples were sonicated for 30 min and then dried under vacuum in a rotary evaporator. Subsequently, the materials were dried overnight at 110 °C, calcined in air at 550 °C for 5 h with a heating rate of 20 °C  $min^{-1}$  and activated by hydrogen reduction (30 Nml  $min^{-1}$ ) in a quartz reactor using a heating rate of 2 °C  $min^{-1}$  up to 450 °C.

Calcined samples (Pd in the form of PdO) were subjected to X-ray Diffraction (XRD) in a Phillips X'PERT MPD diffractometer, using  $Cu-K\alpha$  radiation, within the 10–75° range. The Si/Al ratios and Pd contents were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on a VARIAN Vista AX Axial CCD Simultaneous ICP-AES apparatus after dissolving the samples with  $H_2SO_4$  and HF. Textural properties of the reduced samples (Pd present as Pd<sup>0</sup>) were obtained from argon adsorption–desorption isotherms at 87 K in a Quantachrome Autosorb 1 MP automated gas sorption system. Pore size distributions were determined by the non-local density functional theory (NLDFT), assuming argon adsorption in cylindrical pores. Transmission electron micrographs (TEM) were collected on a Phillips TECNAI 20 microscope equipped with a LaB<sub>6</sub> filament under an accelerating voltage of 200 kV. Pd particle size distributions were derived from a collection of micrographs. The acid properties of the activated catalysts were determined by ammonia temperature programmed desorption (TPD) in a Micromeritics AutoChem 2910 system using the procedure elsewhere described [27].

### 2.2. Hydroprocessing tests

Hydroprocessing reaction tests were carried out in a stirred stainless-steel autoclave reactor. The feed for these reactions

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