

HYDROREFORMING OF LDPE THERMAL CRACKING WAXES OVER Ni/h-BETA CATALYSTS WITH DIFFERENT Ni PARTICLE SIZE OBTAINED FROM DIFFERENT Ni PRECURSORS

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Abstract

Fuel production from polymer wastes by different chemical processes is a novel route for their energy recovery which deserves special attention because of the valuable products obtained. In order to prevent rubber formation, thermal pyrolysis of the polymers must be followed by hydrogenation or hydrotreating of the products, where bifunctional catalysts are necessary. It is expected that hydrogenation activity is inversely correlated to the metal particle size. In this work, three different Ni precursors have been used to obtain Ni particles of different sizes on a hierarchical Beta zeolite. The three catalysts have been tested in the hydroreforming of LDPE thermal cracking waxes indicating that hydrogenation is improved with lower nickel particle sizes.

Keywords: LDPE, fuels, hydrogenation/hydroreforming, Ni particle size, Ni precursors.

1. Introduction

Among all available options for polymer wastes recovery and treatment, chemical processes are the newest and possibly the most interesting ones because of the valuable products obtained. In this sense, fuel production from waste polymers by means of chemical treatments is a novel route for their energy-recovery [1] which reduces disposal rates while obtaining valuable products. Since thermal pyrolysis of the polymers leads to a high amount of olefins which may cause rubber formation in the injection systems of automobiles, further hydrogenation or hydroreforming of the thermal cracking products is required [2].

Hydroreforming is performed over bifunctional catalysts which often consist in small metal particles supported on an acid porous solid. A decrease in metal particle size is meant to increase metal phase dispersion, improving the hydrogenation function. In this work three different nickel precursors (nitrate, acetylacetonate and tris(ethylenediamine)nickel chloride) have been used to impregnate a hierarchical Beta zeolite which is expected to vary the final size of the obtained Ni particles [3]. Smaller metal particles are also expected to improve the hydrogenation of the LDPE thermal cracking product.

2. Materials and Methods

Hierarchical Beta zeolite has been synthesized by a seed silanization procedure using phenylaminopropyl-trimethoxysilane (Aldrich, +97%) [4]. Nickel has been incorporated on the support by impregnation using nickel

nitrate hexahydrate (Aldrich, >98.5%), nickel(II) acetylacetonate (Aldrich, 95%) or tris(ethylenediamine)nickel(II) chloride hydrate (TEDAN, Aldrich, 99.999%). Impregnated samples have been calcined at 550°C in static air and reduced under 30 ml/min hydrogen flow up to 550°C. The catalysts have been characterized by X-Ray diffraction, H₂-TPR, ICP-AES, TEM, NH₃-TPD, N₂ adsorption-desorption at 77K and Ar adsorption-desorption at 87K.

Raw LDPE (Repsol-YPF, MW ~ 416000), was chosen as starting material. An initial charge of 30 g LDPE is thermally cracked in a stainless steel autoclave reactor at 400°C for 90 min under nitrogen atmosphere and 700 rpm stirring. The waxy products are hydroreformed over the chosen catalyst in the same reactor. The hydroreforming is carried out under the following conditions: T = 310°C; t = 45 min; H₂ pressure = 20 bar; catalyst / feed ratio = 1:30. Characterization of the products includes gas chromatography, aromatics measurement by HPLC, Bromine Index, RON number and Cetane Index.

3. Results and Discussion

Hierarchical Beta zeolite is made of aggregates 200-400 nm size. The voids between them, caused by the calcination of the silanization agent, form a secondary mesoporosity which enlarges total pore volume (0.447 cm³g⁻¹). This secondary porosity allows a better dispersion of the Ni particles along the surface than in traditional zeolites.

Figure 1 shows the XRD patterns of the three calcined catalysts. Asterisks point out the NiO main reflections.

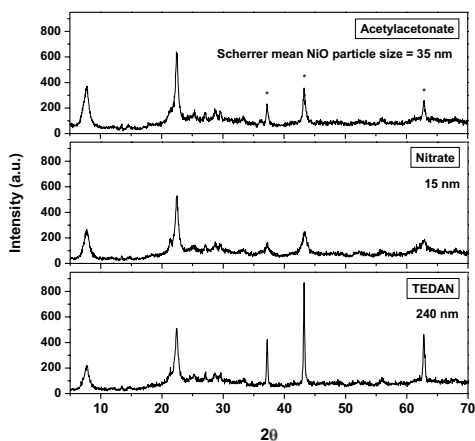


Fig. 1. XRD patterns of the three impregnated and calcined catalysts.

The larger the precursor molecule, the larger the average NiO crystallites obtained, as it is inferred from Scherrer equation applied to the peak at 43°. The big molecules of TEDAN can enter neither the zeolitic micropores nor the small secondary mesopores, so they remain on the large mesopores or the external surface favouring the sintering of the nickel cations during the calcination and activation stages, leading to NiO particles up to 500 nm. This behaviour is also supported by TEM images, which are shown as figure 2. Using TEDAN, extremely large metal particles are formed, being wide areas deprived of nickel.

Differences between the other two precursors are much less significant according to XRD data. Regarding the micrographs, nitrate, the smallest precursor, provides more uniform metal particles, most of them between 10-45 nm, while acetylacetonate, the medium sized allows obtaining very small particles, with a minimum size of 3.4 nm, although the mean size (35 nm) determined by XRD is larger than that with nitrate (15 nm). The presence of large particles may be due to the very high amount of acetylacetonate solution needed to impregnate the zeolite (ten times the pore volume) caused by its low solubility in most solvents, leading to a certain amount of solute in the outer surface. Low solubility is also the reason of the lower final Ni content reached.

The hydroreforming of the LDPE thermal cracking product indicates that the three catalysts show some differences regarding to the hydrogenating function. Using the bromine index of the samples as an indicative parameter, the results are as follows (table 1). All the catalysts are able to hydrogenate the feed in a large extent (> 90%). However, some differences can be observed among catalysts. Comparing the samples prepared with nitrate and TEDAN which contain similar content of nickel (5.5 – 5.95%), it is appreciated that nitrate shows a higher hydrogenation activity, due to its

lower particle size. Likewise, the catalyst prepared with acetylacetonate shows higher hydrogenation activity than the hierarchical Beta prepared with TEDAN, despite its lower nickel content. This is ascribed to the presence of lower size nickel particles.

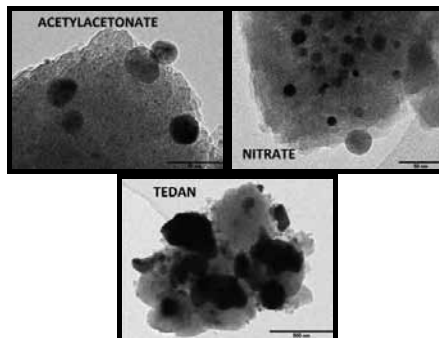


Fig. 2. TEM micrographs of the three catalysts.

Table 1. Nickel content and bromine index of the catalysts in the hydroreforming of LDPE thermal cracking waxes.

	Thermal cracking waxes	Acetylacetonate	Nitrate	TEDAN
Ni content (wt%)	-	3.97	5.95	5.57
Bromine index (g Br ₂ /100 g sample)	54.1	4.5	1.4	5.6

4. Conclusions

Different size Ni particles can be achieved using different precursors. The size of the nickel particles is related to the size and chemical nature of the starting precursor. The lowest bromine index fuel was attained with the hierarchical Beta prepared with nickel nitrate. Consequently, the hydrogenation activity was improved on decreasing the nickel particle size.

References

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