CONVERSION OF LDPE TOWARDS TRANSPORTATION FUELS BY A TWO-STAGE PROCESS USING Ni/Al-SBA-15 AS CATALYST

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Abstract

The effect of the Si/Al atomic ratio of mesostructured Ni/Al-SBA-15 catalysts has been studied in the hydroreforming of the oil resulting from the thermal cracking of low-density polyethylene. The size of the nickel particles over Al-SBA-15 increased with the Si/Al atomic ratio of the supports. The enhancement of the Si/Al atomic ratio of the Al-SBA-15 increased the share of light diesel (C_{13} – C_{18}) hydrocarbons, reaching a 40% for Si/Al = 100. All the catalysts allowed obtaining a high hydrogenation degree (87%) and the fuels contained a low share of aromatics (< 5%)

Keywords: *LDPE, fuels, hydrogenation/hydroreforming, SBA-15.*

1. Introduction

The waste plastics cause serious environmental problems. The main components of the plastic waste were polyolefins (LDPE, HDPE and PP). Catalytic conversion of polyolefin plastic wastes into fuels over acid catalysts catalysts is one of the technologies that is receiving increased attention due to the interesting products obtained (gasoline, diesel, fuel, etc)[1,2]

In previous works, a two-stage process comprising thermal cracking of the polyolefins followed by catalytic hydroreforming was devised. This process allows the high content of olefins usually obtained in the thermal cracking of the plastics to be removed. Additionally, it enables to tailor the selectivity towards the desired products. In this regard, high selectivity towards gasolines (> 55%) was obtained previously over Ni/h-Beta catalyst [3,4].

In this work, we have studied another catalyst (Ni/Al-SBA-15) varying its Si/Al atomic ratio. Unlike Ni/h-Beta, this catalyst showed remarkable selectivity toward diesel fuels due to its mild acidity, that was tuned by adjusting the Si/Al atomic ratio.

2. Materials and Methods

Al-SBA-15 was obtained by a post-synthesis alumination method [5]. Hence, solution A formed by 100 mL of an aqueous solution of $AlCl_3 \cdot 6H_2O$ was left under stirring at 60 ºC for 1h. Solution B, formed by 100 mL of an aqueous TMAOH was mixed and added to solution A. The molar hydrolysis ratio [TMAOH]/[Al] was 2. The resulting mixture was heated at 60ºC for 1 h. 2 g of pure SBA-15 was added at room temperature under stirring for 5 h. The obtained solid products were separated by filtration, dried overnight at 110 ºC and calcined in air at 550 ºC for 5h. The catalyst Ni/Al-SBA-15 was prepared by the incipient wetness and sonication method with a nickel nitrate solution using a solution volume/ pore volume ratio of 1.

LDPE was thermally cracked at 400ºC for 90 min. The obtained oils were a mixture of C_5 – C_{40}, formed chiefly by n-paraffins + olefins and used as feed of the subsequent hydroreforming stage. The hydroreforming reactions were performed in an autoclave at 310 ºC under 20 bar of hydrogen for 45 min using an oil/catalyst mass ratio=30.

3. Results and Discussion

Table 1 summarizes the main textural properties of the catalysts Ni/Al-SBA-15 obtained varying the Si/Al atomic ratio within the 15 – 100 range. All the catalysts showed BET surface areas above 400 m^2 g^{-1}, pore volumes higher than 0.6 cm^3 g^{-1} and average pore sizes within 8 – 10 nm. Likewise, the nickel content of the catalysts was within 6 – 10% (see table 2). Figure 1 illustrates the TEM micrographs of Ni/Al-SBA-15-15 and Ni/Al-SBA-15-100, wherein it is clearly seen that the size of the nickel particle increased with the Si/Al atomic ratio.

Table 1. Physicochemical Properties of the catalysts.

Catalyst	BET (m^2/g)	Pore Volume (cm^3/g)	Average Pore Size (nm)
Ni/Al-SBA-15-15	411	0.71	8.3
Ni/Al-SBA-15-30	440	0.62	10.6
Ni/Al-SBA-15-50	548	0.71	8.2
Ni/Al-SBA-15-70	492	0.66	8.2
Ni/Al-SBA-15-100	527	0.68	10.7

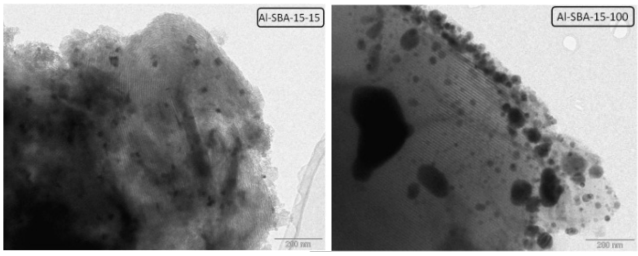

Fig. 1. TEM micrographs of the catalysts Ni/Al-SBA-15-15 and Ni/Al-SBA-15-100.

Figure 2 shows the yields by groups obtained in the hydroreforming of the product from LDPE thermal cracking over the different Ni/Al-SBA-15 catalysts. The total yield of liquid hydrocarbons was roughly 95%, which constitutes a rather remarkable amount.

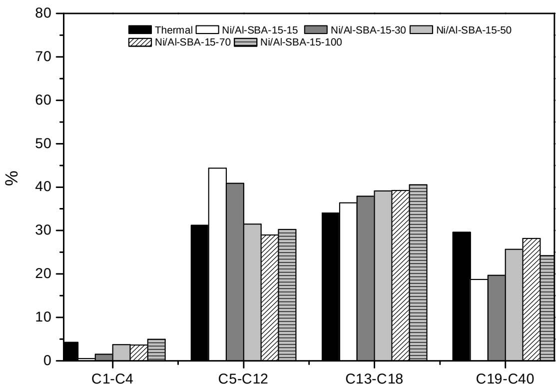

Fig. 2. Effect of the ratio Si/Al of the Ni/Al-SBA-15 catalysts in the hydroreforming of the oil from LDPE thermal cracking

The increase of the Si/Al atomic ratio of the catalyst decreased the gasoline selectivity and increased the selectivity to C_{13}-C_{18} light diesel hydrocarbons, reaching 40% for a Si/Al atomic ratio of 100. Additionaly, the total yield of light and heavy diesel hydrocarbons (C_{13} – C_{40}) amounts to 65% for Si/Al atomic ratios above 50. The main products obtained in the gasoline fraction are normal paraffins (60 - 80%%) while isoparaffins account for 15%. In order to check the degree of hydrogenation of the olefins present in the reaction medium, the bromine index of the liquid products was calculated. The thermal cracking of LDPE contained a great deal of olefins (54g Br_2/100 g of sample). All the catalysts exhibited bromine indexes around 6, which implies a reduction of 87% of the olefinic double bonds of the feed (see table 2). The aromatic content in the fuels was low in all the cases, always below 5%. .

Table 2. Nickel content, aromatics and bromine index of the catalysts in the hydroreforming of the oil form LDPE thermal cracking.

Catalyst	Bromine index (g Br_2/100 g of sample)	Aromatics (%)	Ni content (%w)
Ni/Al-SBA-15-15	7.4	4.1	10.9
Ni/Al-SBA-15-30	6.8	4.9	6.1
Ni/Al-SBA-15-50	6.8	4.2	10.8
Ni/Al-SBA-15-70	6.6	3.7	9.5
Ni/Al-SBA-15-100	7.5	3.7	9.8

4. Conclusions

The size of nickel particle over Ni/Al-SBA-15 catalysts is heterogeneus and it increased with the ratio Si/Al. The increase of the Si/Al atomic ratio of the catalyst decreased the gasoline selectivity and increased the C_{13}-C_{18} diesel hydrocarbons selectivity, reaching a 40%. The olefins were largely hydrogenated (around 87%) and the aromatic content of the fuels was rather low (< 5%).

5. References

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