

CATALYTIC CRACKING OF POLYETHYLENE OVER HIERARCHICAL H-ZSM-5 ZEOLITES WITH DIFFERENT PROPORTION OF MICRO- AND MESOPOROSITY

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Abstract

A variety of H-ZSM-5 zeolites with hierarchical porosity, that is, containing both the characteristic zeolite micropore system and additional mesoporosity were prepared according to the method of crystallization from silanized seeds. These materials differing in crystallinity and textural properties were compared with nanocrystalline H-ZSM-5 samples, and tested in the catalytic cracking of low density polyethylene (LDPE). The selected catalysts range from fully crystalline according to XRD and FTIR to amorphous ones. As crystallinity diminishes, microporosity decreases, BET surface area increases (up to 1085 m²g⁻¹) and secondary mesoporosity appears, with pore diameters centered at 20 and 400 Å. Cracking reactions were carried out employing really mild conditions: 340 °C and plastic/catalyst mass ratio of 100. Turnover frequencies values (TOF) from 0.03 to 0.90 were attained, the most active materials being those combining high crystallinity and acid sites fully accessible through the additional mesopores generated (20-70 Å). The selectivity depends on the catalyst employed but the major products were C₁-C₅ hydrocarbons, percentages always higher than 50% being attained. The amount of middle distillates (>C₁₃) was always below 2%.

Keywords: catalytic cracking, hierarchical zeolite, ZSM-5, silanized seeds.

1. Introduction

Among the number of alternatives existing in the field of feedstock recycling, catalytic cracking over different solid catalysts has attracted special attention in the last years [1]. Particularly, it is possible to obtain valuable hydrocarbon mixtures, with remarkable activities and very high selectivities towards light olefins employing nanocrystalline H-ZSM-5 zeolite, due to its strong acidity and high proportion of external surface area. Moreover, hierarchical nanocrystalline H-ZSM-5, containing a bimodal pore system with an important mesoporosity additional to the conventional zeolite micropore system, has been synthesized according to the strategy of crystallization from silanized seeds [2] and has proven its higher activity in the catalytic cracking of polyolefins with respect to the traditional nanocrystalline H-ZSM-5 [3]. These results were ascribed to the good acid properties and higher proportion of external surface area (intercrystal mesoporosity) of the hierarchical zeolites. In this work, a number of hierarchical H-ZSM-5 zeolites, containing different proportions of zeolite micropores and additional mesopores, have been prepared. These materials have been compared with two nanocrystalline H-ZSM-5 samples, and tested in the catalytic cracking of low density polyethylene (LDPE), with the aim to ascertain the importance of the mesoporosity in the catalytic activity of the hierarchical catalysts.

2. Materials and Methods

Synthesis methods published elsewhere were applied in order to prepare the hierarchical [2] and nanocrystalline [4] H-ZSM-5 zeolites. The experimental conditions were modified and adjusted in order to obtain zeolites with different physicochemical and textural properties. The samples were characterized by means of conventional techniques: XRD, FTIR, N₂ adsorption-desorption isotherms at 77 K, Ar adsorption-desorption isotherms at 87 K, TEM, NMR, ICP-AES, TPD, TG and elemental analysis.

The cracking reactions of low density polyethylene (LDPE) were carried out in a stainless steel batch reactor provided with a screw stirrer. In a typical experiment, a mixture of 10 g of plastic and 0.10 g of catalyst (P/C = 100) were loaded into the reactor. Next, the reactor is heated up to the reaction temperature (340 °C) that was maintained for 2 h. The volatile products are swept from the reactor by a continuous nitrogen flow. Subsequently, liquid and gaseous products are separated in a condenser cooled by an ice/water mixture and collected for GC analysis. Conversions have been calculated taking into account only the products that leave the reactor with the N₂ stream, the remaining residue being not considered as a reaction product. The activity was

calculated as (mass of plastic converted) (mass of aluminium in the catalysts)⁻¹ s⁻¹.

3. Results and Discussion

Ten H-ZSM-5 zeolites with different textural properties were synthesized and tested in the catalytic cracking of LDPE. Table 1 summarizes the main physicochemical properties of the calcined samples. According to XRD and FTIR data (not shown), the crystallinity decreases from sample 1 to sample 10, being samples 9 and 10 practically amorphous materials. This fact is in agreement with the reduction in the surface of the zeolite micropores (S_{ZMP}), observed in Table 1, from sample 1 to 10. Moreover, as the crystallinity (and S_{ZMP} values) of these samples diminishes, the values of BET surface area (S_{BET}) and secondary porosity ($S_{SP} = S_{BET} - S_{ZMP}$) increase. Consequently, the decrease of XRD and FTIR crystallinity of the samples is accompanied by the parallel development of mesoporosity. While both nanocrystalline samples 1 and 2 show mainly a strong maximum centered at 5.5 Å in the pore size distribution, corresponding to the dimension of the micropores of ZSM-5 zeolites, hierarchical H-ZSM-5 zeolites (from 3 to 8) exhibit also mesoporosity within 20-70 Å. Finally, the micropore peak practically disappear in amorphous samples 9 and 10, arising however a huge peak centered at 400 Å, which could be assigned to interparticle mesoporosity. As inferred from Table 1, all the samples were prepared with Si/Al atomic ratios in the range 17-36, according to ICP analyses, and practically the whole of aluminium was incorporated into its framework (from ²⁷Al MAS-NMR experiments, not shown). The temperature maximum (T_{max}) of the NH₃ desorption (calculated from NH₃ TPD measurements) shows a roughly decreasing trend from sample 1 (~290) to sample 10 (~260 °C). Consequently, the generation of secondary porosity implies a decrease in the acid strength of the acid sites.

Table 1. Physicochemical and textural properties.

Sample	Si/Al	T_{max} (°C)	S_{BET} (m ² /g)	S_{ZMP} (m ² /g)	S_{SP} (m ² /g)
1	36	391	420	346	74
2	29	395	409	352	57
3	34	385	553	311	242
4	31	363	559	293	266
5	36	333	675	233	442
6	35	361	798	180	618
7	33	321	655	161	494
8	28	302	792	57	735
9	17	265	888	38	850
10	33	269	1085	19	1066

All the later samples were tested in the catalytic cracking of LDPE employing really mild conditions (340 °C and P/C=100), and the results obtained are depicted in Fig. 1. The highest conversion (86%) and turnover frequency (TOF) values (0.90 s⁻¹) are attained employing the sample 3, decreasing these parameters along the series of hierarchical H-ZSM-5 samples (3-10). The two

nanocrystalline samples (1 and 2) show conversion and TOF values around 25-50% and 0.30-0.45 s⁻¹, respectively, clearly higher than those obtained with the samples 8 to 10. The selectivity patterns obtained are in line with the typically obtained over the H-ZSM-5 zeolite, which is known to yield mainly light hydrocarbons (below C₁₃). The major products are C₁-C₅ hydrocarbons, with percentages in the range 55-65% for samples 1 to 7, and higher than 80% for samples 8 to 10. The proportion of hydrocarbons heavier than C₁₃ is always below 2%.

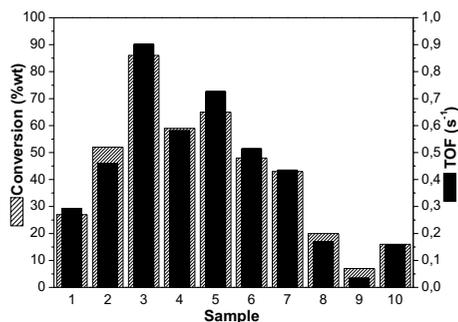


Fig. 1. Catalytic cracking of LDPE over the calcined samples ($T = 340^{\circ}\text{C}$, $t = 2$ h, $P/C = 100$).

4. Conclusions

The catalytic performance of the different samples is explained in terms of the compromise between the acid strength and the accessibility of the acid sites (development of mesoporosity). Hence, the intermediate activity of the two nanocrystalline H-ZSM-5 samples is due to the presence of fully crystalline acid sites but not very accessible through their interparticle mesoporosity. In contrast, the remarkable activity of hierarchical H-ZSM-5 sample 3 can be ascribed to the presence of highly crystalline acid sites fully accessible through its mesopores (20-70 Å), enabling the bulky molecules of LDPE to diffuse. Likewise, the progressive loss of strength of the acid sites along the series of hierarchical H-ZSM-5 materials (4-10) explains the observed decrease of the activity, despite the progressive development of secondary porosity.

References

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