

On the positive influence of Pd species on low-density polyethylene cracking

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Abstract

Microporous 12-ring zeolite Beta was impregnated with palladium and evaluated in the cracking of low-density polyethylene (LDPE) cracking. In addition to the catalytic measurements the materials were characterized by X-ray diffraction, chemical analysis and nitrogen adsorption, electron microscopy, and FT infrared spectroscopic studies pyridine and CO adsorption. In addition to TGA catalytic studies, the operando IR studies were furthermore performed to follow the aromatic species formation. Deposition of palladium on microporous zeolite BEA improved the catalytic activity and selectivity towards C₂-C₄ fraction.

Keywords: LDPE cracking, zeolite, in situ and operando IR spectroscopy

1. Introduction

Thermal cracking is one of the simplest methods of recycling plastic waste where it allows obtaining hydrocarbons with a wide range of molecular weight. Nevertheless, the high temperature necessary for polymer cracking, low product quality and efficiency are the main disadvantages. The effective methods of plastic waste treatment include catalytic pyrolysis using zeolites as catalysts. The zeolites (HZSM-5, USY, H-Beta, etc.) have been of special interest due to their acidic properties and porous structure. Acid sites, more precisely their nature, strength as well as distribution are the key parameters affecting the rate, efficiency and selectivity of catalytic pyrolysis. The use of the acid catalyst is reflected in the appearance of C₂-C₄ olefins, as usually the higher strength of acid sites, the more effective is the cracking of polymer chains as reported in works Tarach K.A. et al and Pyra K. et al..

2. Experimental

The parent zeolite NH₄Beta, Si/Al = 22, was purchased from Zeolyst (CP814C). The synthesis of the catalysts containing palladium was conducted by adding an appropriate amount of the zeolite to a specified volume of a PdCl₂ solution based on a previously developed method by Hasik M. et al.. Elemental Si and Al concentrations in the materials were determined by the ICP OES method using an Optima 2100DV

(PerkinElmer) spectrometer. Nitrogen sorption measurements at -196 °C were performed on a Quantachrome Autosorb-1-MP gas sorption apparatus according to procedure given by Tarach K.A. et al. and Pyra K. et al.. Transmission electron microscopy (TEM) pictures were taken from a Tecnai Osiris microscope (FEI) with a X-FEG Schottky field emitter operated at 200 kV. Scanning transmission electron microscopy (STEM) images were obtained using a high-angle annular dark-field (HAADF) detector. The IR spectra were recorded with resolution of 2 cm⁻¹ with a Bruker Vertex 70 spectrometer. The concentrations and strength of the acid sites were determined in the Py-gas sorption experiments while the nature of the Pd species was evaluated in the CO sorption (Tarach K.A. et al. and Pyra K. et al.). The low density polyethylene (LDPE) decomposition was studied in an operando system connected to a flow set-up as well as by thermogravimetric analysis, both described in detail by Tarach K.A. et al. and Pyra K. et al..

3. Results and Discussion

The XRD patterns of the microporous zeolite Beta exhibited well resolved reflections representative for BEA structure, which was fully preserved after palladium deposition (Fig. 1 c). The N₂-isotherm for zeolite BEA confirmed its microporous character (isotherm type-I). The pH in the range of 3-4 applied during palladium deposition can be responsible for the slight improvement of micropore and mesopore volume (Fig. 1). The total concentrations of acid sites (C_B + C_L) determined by pyridine in Beta match well with the values of the Al content obtained from the chemical analysis (Fig. 1 f), thus each Al atom is supposed to form either an acidic Si(OH)Al group or a Lewis acid site, both accessible to the Py molecule. The Pd-deposition did not perturb the strength of the bridging hydroxyls, obtained from Py thermo-desorption and measured as the values of the frequency shifts $\nu_{\text{CO}\dots\text{OH}}$ of the band of the Si(OH)Al groups interacting with the CO molecule. The CO sorption evidenced also the presence of the linear Pd⁺-(CO) (2100-2000 cm⁻¹) and Pd⁰-CO carbonyls, both linear and bridged (IR bands below 2000 cm⁻¹) (Chakarova K. et al.). The intensity of the bridged carbonyls bands was negligible.

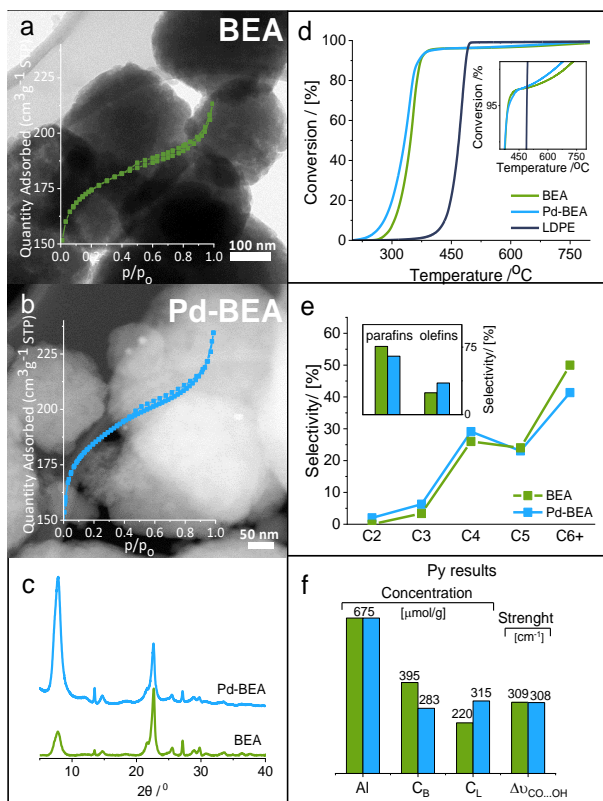


Fig. 1. Structural-textural characteristics of the zeolites studied: TEM and STEM micrographs, N₂ adsorption–desorption isotherms (a,b), XRD patterns (c). The results of the quantitative Py sorption expressed as the total number of $\mu\text{mol Al}$ per gram of zeolite, number of Bronsted (C_B) and Lewis acid sites (C_L) as well as the strength of protonic sites as the $\Delta v_{\text{CO}\dots\text{OH}}$ values (f). Conversion curves of LDPE cracking, including the thermal cracking and selectivities (d, e).

The polyethylene catalytic cracking over the zeolites are given in Fig. 1 d, where the LDPE conversion is plotted as a function of temperature. For both samples, the conversions are higher than 95 % above 420 °C. The zeolite BEA improves the catalytic performance by lowering the conversion temperature in ca. 120 °C, compared to thermal cracking. The bifunctional catalyst Pd-BEA, further enhanced the activity by lowering the conversion in whole temperature range by ca. 10-30 °C, compared to zeolite BEA. This effect can be related to high hydrogenation efficiency of the bifunctional catalyst especially at lower temperatures (220-320 °C). The polymer cracking selectivity provided higher amount C₂-C₄ fraction at the expense of the C₅₊ fraction is also accompanied by higher selectivity to olefins.

Interestingly, for Pd-loaded zeolite at 650 °C the slope of the conversion starts to increase evidencing the consumption of coke deposit due to its gasification. The water molecules required for this process can originate from both the residual water and/or from dehydroxylation of the zeolitic hydroxyls. Doping the catalyst with Pd decreases the temperature of aerobic burning of coke to allow catalyst surface regeneration.

4. Conclusions

Deposition of palladium on a microporous zeolite BEA enhanced the catalytic activity by lowering the conversion temperature in ca. 10-30 °C, and an improving the selectivity by providing a higher amount of C₂-C₄ fraction. The decrease of the temperature of coke aerobic burning for Pd-BEA would facilitate catalyst surface regeneration.

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