Bottom-up synthesized hierarchical Beta zeolites as the catalysts for low-density polyethylene cracking

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Abstract

Improving mass transport in zeolites Beta by bottom-up hierarchization was aimed at preserving their native microporous acidic characteristic and finally demonstrating their applicability in LDPE catalytic pyrolysis, in contrast to top-down modified analogues.

Keywords: hierarchical zeolites Beta, LDPE cracking, IR spectroscopy

1. Introduction

The major problem faced nowadays is a large amount of plastic waste, which is usually stored up and as well as, unfortunately, deposited in water. Currently, the most common method of its utilization is thermal cracking; however, numerous paper points to the catalytic pyrolysis as a more efficient way for plastic waste utilization. Among the variety of the potential catalyst, zeolites are supreme materials due to their microporous structure and tunable acidic properties. The presence of micropores solely in zeolite grain often imposes diffusion limitations due to restricted access of polymer chains to acid sites and slow intracrystalline transport of the product molecules within the micropore environment. Pyra et al. have reported that fabrication of mesopores in zeolite Beta benefits in LDPE cracking when the strength of protonic acid sites remained above the level of 80% of the original one. When the acid strength is further lowered, the mesoporosity effect fails. In this work, the zeolite Beta hierarchization was aimed to improve the reagents transport with preserved acidic characteristics, especially in the manner of the strength of Si(OH)Al hydroxyls.

2. Experimental

The zeolite Beta seeds were prepared from the mixture with a molar composition of SiO_2: $0.02Al_2O_3$: 0.028 Na_2O: 0.6TEAOH: 0.2HCl: $20H_2O$. 14.7 mL of 25% tetraethylammonium hydroxide (35%) was mixed with 2.25 mL of 3.70 M HCl. Then, 2.5 g fumed silica was added under vigorous stirring. After 30 min, 0.1906 g of $NaAlO_2$, dissolved in 2.9 mL water was added, and the reaction mixture was stirred for 30 min. The obtained gel was aged at 150 °C for 22 h under static conditions. Microporous Beta (Beta_0) was synthesized according to the procedure described above without modification step. The Beta seed mixture after cooling was modified and crystallized. Beta_T was obtained from zeolite Beta seeds precursor by its acidification using concentrated hydrochloric acid. 5 mL of concentrated HCl (37%) was added to 18 mL of Beta seeds solution under vigorous stirring, lowering the pH of the solution to below 1. The obtained mixture was stirred for 1 h and then crystallized. Beta_G was obtained from Beta seeds which were functionalized with (3-Glycidyloxypropyl) trimethoxy-silane, used in a molar percentage of 5% relative to the total amount of silicon in the seeds gel. The functionalization of Beta seeds with the organosilane took place under reflux at 90 °C, for 6 h, with stirring. The obtained mixture was crystallized. The Beta_C was obtained by adding 9 mL of 19.28 wt.% aqueous solution of cetyltrimethylammonium bromide and 1.12 ml of 3.70 M HCl to the zeolite beta precursor solution under stirring, whereupon stirring was continued for 1h. The obtained mixture was crystallized. The crystallization of all samples was performed at 150 °C for 3 days. The obtained materials were filtered, washed, dried and calcined. The H-forms were obtained by four-fold ammonium ion-exchange with 0.5 M NH_4NO_3 at 60 °C for 1 h with subsequent filtration, washing, drying at room temperature, and calcination at 550 °C for 5 h, in order to obtain the active proton-form.

Elemental Si and Al concentrations in the materials were determined by the ICP OES method using an Optima 2100DV (PerkinElmer) spectrometer. Powder X-ray diffraction patterns were recorded on the Philips Bruker D8 Advance diffractometer using Cu Ka radiation (λ=1.54056 Å). The N_2 adsorption/desorption isotherms were measured at –196 °C on the Quantachrome Nova 1000 sorptometer. The samples were outgassed at 300 °C prior to the measurement. The specific surface area was determined using the BET method, whereas the external surface area and micropore volume were calculated by the t-plot method. The total volume of pores was assessed using the single point model (at p/p_0 = 0.98). The BJH pore size distributions were derived from the adsorption branch. The IR spectra were recorded with a 2 cm^{-1} resolution with a Bruker Vertex 70 spectrometer. The concentrations and strength of the acid sites were determined in the Py-gas sorption experiments basing on the reports of Pyra K. et al. and Tarach K.A. et al.. The low-density polyethylene (LDPE) decomposition was studied by thermogravimetric analysis *(Pyra K. et al. and Tarach K.A. et al.)*.

3. Result and Discussion

The XRD patterns of the microporous zeolite Beta and its modified counterparts exhibited well-resolved reflections representative for BEA structure (Fig. 1A). Both zeolite Beta_0 and Beta_G showed isotherm type-I evidencing their purely microporous feature, in contrast to micro-/mesoporous properties of the zeolites Beta_C and Beta_T described by the type-IV isotherm (Fig. 1B, Table 1). In addition, the isotherm of Beta_T displayed additionally a sharp increase in the adsorbed volume at high relative pressures ($p/p_0 > 0.8$) associated with the secondary mesopores from the spacing among the nanoparticles.

Table 1. Textural and acidic properties of zeolites Beta.

Sample	Si/Al	S_{meso}	S_{micro}	BAS*	Py_{500}/Py_0*
		m^2/g	m^2/g	µmol/g	
Beta_0	19	98	362	380	0.94
Beta_T	17	233	206	233	0.90
Beta_G	17	179	315	340	0.95
Beta_C	23	399	153	323	0.81

*BAS: Brønsted acid sites concentrations and Py_{500}/Py_0 expressing the strength of Brønsted sites, both derived from quantitative IR studies of Py sorption (*Pyra K. et al. and Tarach K.A. et al*.).

Fabrication of an additional mesoporosity in the bottom-up synthesised zeolites Beta is represented by the enhanced values of both the mesopore surface area and the mesopore volume. The Beta_T and Beta_C contributed to the most developed mesopores surface area which is clearly manifested as the highest population of isolated silanols (the 3745 cm^{-1} band) located on the mesopore surface (Fig. 1C). Both Lewis and Brønsted acid sites are involved in the polymer cracking by successive β-scissions generating fragments with lower molecular weights. As previously reported (*Pyra K. et al.*) the enhanced number of acidic sites available for LDPE is not as important as the number of highly acidic Si(OH)Al groups (the 3605 cm^{-1} band) hosted in the internal voids of the microporous environment. Indeed, for Beta_T the number of protonic sites was reduced, however, their strength is still preserved. The bottom-up hierarchization strategy appears more favour than desilication since it does not perturb negatively the acidic properties of resulting materials. The Brønsted acidic sites present in the studied mesoporous zeolites Beta are of the same strength as the protonic sites in the purely microporous zeolitic materials. The facilitated diffusion provided by the mesopore system significantly facilitates the access of branched LDPE chains to the highly acidic Si(OH)Al sites located in the micropores allowing a reduction of the $T_{50\%}$ value by *ca.* 100 °C in comparison to the thermal cracking and *ca.* 20 °C with respect to microporous Beta_0 (Fig. 1D). All the mesoporous zeolites studied are more catalytically active towards cracking since they provide the Si(OH)Al groups of high strength. The Beta_G benefits the LDPE cracking in spite of a slight mesoporosity development coupled, however, with the presence of protonic sites of the highest strength.

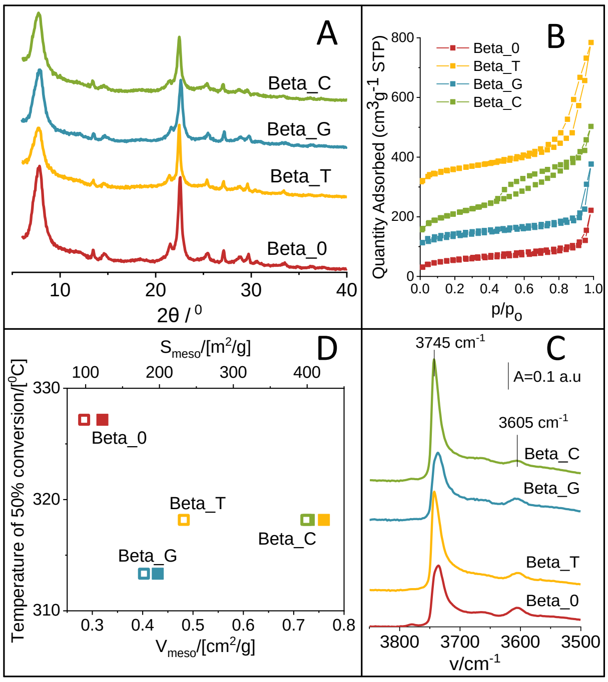

Fig. 1. Structural-textural characteristics of the zeolites studied: XRD patterns (A), N_2 isotherms (B), IR spectra in the region of the O-H stretching vibrations (C), and dependence of temperature of 50 % conversion to V_{meso} (solid symbols) and S_{meso} (open symbols) (D).

4. Conclusions

The preserving intrinsic zeolite properties in mesoporous zeolites synthesised by bottom-up approach benefits in lowering LDPE cracking temperature with respect to microporous analogue. It is in contrast to hierarchical zeolite Beta obtained by caustic treatment where a high mesoporosity achieved is accompanied by a strong decline in acidic properties.

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References

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