

Solid acids for catalytic pyrolysis of waste plastic to produce olefins

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Introduction

Global annual polyethylene production accumulates to about 80 million ton and the majority is used for short-lived products, such as packaging, which after disposal represent an enormous environmental burden. Due to its easy availability, high energy density and defined chemical composition, thermocatalytic pathways offer attractive means for depolymerization of waste plastic into olefins, which can be used as liquid fuels or added value chemicals for chemical or polymer industry. By modifying acid strength, pore size and type of solid acids, selectivity for lower olefins, coke, petroleum and diesel-like olefin fractions can be favored [1].

Materials and Methods

Natural aluminosilicate containing primarily montmorillonite (*M*) was subjected to H_2SO_4 acid treatments (*MSx*, where *x* denotes the acid wt. % concentration), boiling under reflux, followed by washing and drying) and ion exchange with NH_4NO_3 (*MI*) in order to increase available specific surface area, create mesoporosity and acidity by substitution of charge compensating ions, such as Na, Ca, Fe and K.

Amorphous silica alumina (*ASA*) (synthesized by deposition-precipitation of aluminum nitrate by urea over a commercial silica gel, followed by drying and calcination for 12 h at 800 °C), sulfated and fluorinated $\gamma-Al_2O_3$ (*SA* and *FA*, prepared by incipient wetness impregnation of commercial $\gamma-Al_2O_3$ with H_2SO_4 or NH_4F , followed by thermal decomposition of NH_4F , respectively) and a commercial HZSM-5 zeolite (Si/Al= 14.3) were also tested for PE depolymerization. Prepared catalysts were characterized by N_2 sorption, SEM/EDX, DRIFTS, N-propylamine TPD and XRD techniques. Tests were performed in a TG/DSC apparatus by thoroughly mixing PE and catalyst powders and heating with a 20 °C ramp to 900 °C in N_2 atmosphere.

Results and Discussion

Acid treatment of montmorillonite aluminosilicates (initially containing 6.3 wt. % Al) with H_2SO_4 was successfully employed to increase the BET specific surface area for about 5 times (from 36 to 130-150 m^2/g , depending on acid concentration) and modify the pore diameter and total pore volume (Table 1). It also resulted in substantial removal of Na, K, Ca, Mg and Fe (40-90 % removal). By prolonging the acid treatment, as well as ion exchange, progressive sample dealumination was observed (15-70 % of aluminum was leached). Loss of aluminum (Si/Al for *M* : *MS5* : *MS10* : *MS80* = 4.7 : 7.6 : 7.8 : 14.6) reflects itself also in the FTIR spectra (Figure 1a), which show disappearance of Si-O-Al bending (520 cm^{-1}) and a progressive shift of the absorption band at about 1010 cm^{-1} to higher wavenumbers with intensification of acid treatment. The latter, characteristic of asymmetric stretching of SiO_4 tetrahedron units, is known to shift to higher wavenumbers with increased Si/Al ratios [2].

Observed activity in PE depolymerization (Figure 1b) generally correlates with the abundance of surface acidic sites. The discrepancy in case of HZSM-5 is very probably caused

by mass transfer limitations, originating from microporosity of the material. On the contrary to expectations, various acid treatments of natural aluminosilicate resulted in improved catalytic performance only at lower temperatures. Compared to untreated sample, inferior activity was measured at higher temperatures, which is due to a considerable loss of octahedrally coordinated aluminum. The presence of the latter is the prerequisite for activity, as it enables the formation of highly acidic bridging hydroxyl or sulfonic surface functional groups.

Table 1. Morphological properties, total acidity and temperature of 50 % PE conversion for selected differently modified natural zeolites and synthetic solid acids.

Sample	BET (m^2/g)	V_{tot} (cm^3/g)	D_{av} (nm)	Total acidity (mEq/g)	T_{50} (°C)
SA	121	0.59	19.7	0.622	330
HZSM-5	349	0.16	0.55	0.781	339
ASA	222	0.54	9.7	0.485	364
FA	156	0.75	19.2	0.341	403
M	36	0.07	7.8	0.185	435
MS5	106	0.09	4.2	0.355	459
MI	31	0.06	8.6	0.104	461
PE	/	/	/	/	484

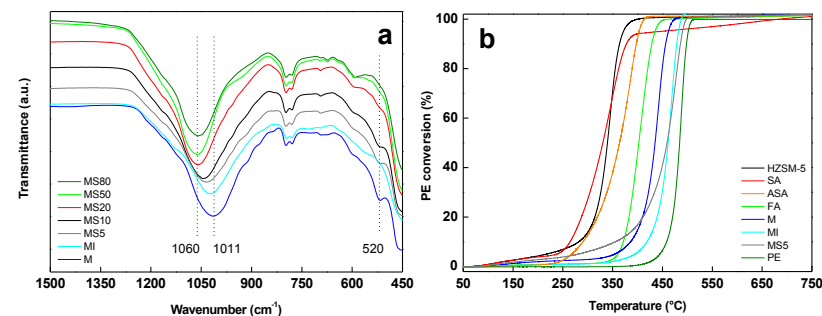


Figure 1. a) FTIR spectra of natural aluminosilicates treated with different concentrations of H_2SO_4 and b) PE depolymerization activity.

Significance

The natural and abundant aluminosilicate exhibits moderate activity for PE depolymerization in comparison to synthetic materials. Acid treatment of the former successfully increases activity at lower temperatures; however, reaction rates decrease with an increase of temperature due to excessive loss of aluminum. Sulfonation and fluorination substantially improved catalytic performance of synthetic alumina based catalysts due to newly generated acid sites.

References

- Elordi, G., Olazar, M., Lopez, G., Castano, P., Bilbao, J. Appl. Catal. B **2011**, 102, 224.
- Wu, G., Wu, W., Wang, X., Zan, W., Wang, W., Li, C. Microporous Mesoporous Mater. **2013**, 180, 187.