

KINETICS OF CATALYTIC DEPOLYMERIZATION OF WASTE PLASTICS TO OLEFINS OVER NATURAL ALUMINOSILICATES

*T. Tomše¹, J. Grdadolnik¹, Š. Božič¹, B. Erjavec¹, M. Zabilskiy¹,
P. Djinović¹, G. Berčič², A. Pintar¹*

¹Laboratory for Environmental Sciences and Engineering, Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

²Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

E-mail: albin.pintar@ki.si

ABSTRACT

Different chemical modifications were performed to the natural aluminosilicate Montanit300[®] in order to improve its catalytic activity in polyethylene (PE) depolymerization. Performance of so prepared catalysts was compared to established solid acid catalysts, such as HZSM-5 and amorphous silica-alumina. DRIFTS and pyridine TG characterization revealed mild acid treatment and aluminum grafting as successful approaches in increasing acid site density through impurity removal and specific surface area increase. Mesoporous catalyst structure that allows facile diffusion through its pore network, together with high density of Brønsted acid sites, was found to be of crucial significance in order to obtain high catalytic activity. The pyrolysis kinetics of pure PE and physical mixtures of PE and catalysts were investigated, and the measured data were confronted with various kinetic models.

Keywords: acid catalyst, fuel-grade hydrocarbons, PE depolymerization, kinetics.

INTRODUCTION

Global annual polyethylene (PE) production accumulates to about 80 million ton and the majority is used for short-lived products, such as packaging, which 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 plastics to olefins, which can be used as liquid fuels or added value chemicals. Natural aluminosilicates are abundant and cheap, exhibit moderate acidity and have been extensively used before the discovery of synthetic zeolites as catalytic cracking catalysts for hydrocarbons [1]. Chemical and morphological modifications to improve their activity and selectivity provide an attractive approach to liquid hydrocarbon production from PE depolymerisation [2]. In this study, reaction kinetics of PE depolymerization over variously prepared catalyst samples was investigated in detail, too.

EXPERIMENTAL

Natural aluminosilicate containing primarily clinoptilolite and heulandite (Montanit300[®], M) was subjected to H₂SO₄ acid treatments, boiling under reflux, followed by washing and drying (MS_x, where x denotes the acid wt. % concentration), and ion exchange with NH₄NO₃ (MI), in order to increase specific surface area, create mesoporosity and acidity by substitution of charge compensating ions, such as Na, Ca, Fe and K. In addition, M solid was after treatment with HCl grafted with 10 wt. % of Al (MAI sample).

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 γ -Al₂O₃ (SA and FA, prepared by incipient wetness impregnation of commercial γ -Al₂O₃ with H₂SO₄ or NH₄F, followed by thermal decomposition of NH₄F, respectively) and a commercial HZSM-5 zeolite (Si/Al=14.3) were

also tested for PE depolymerization. The synthesized catalysts were characterized by N₂ physisorption, SEM/EDX, DRIFTS, TG pyridine, N-propylamine TPD and XRD techniques.

Catalytic tests were performed in a TG/DSC apparatus (Perkin Elmer, model STA 6000) by thoroughly mixing PE and catalyst powders in various ratios and using different heating ramps up to 900 °C in N₂ atmosphere.

RESULTS AND DISCUSSION

Acid treatment of M sample (initially containing 6.3 wt. % Al) with H₂SO₄ was successfully employed to increase the BET specific surface area (S_{BET}) for about 5 times (from 36 to 130-150 m²/g, depending on acid concentration) and modify the pore diameter (D_{av}) and total pore volume (V_{tot}) (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 Al (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 SiO₄ tetrahedron units, is known to shift to higher wavenumbers with increased Si/Al ratios [3].

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

Sample	S_{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

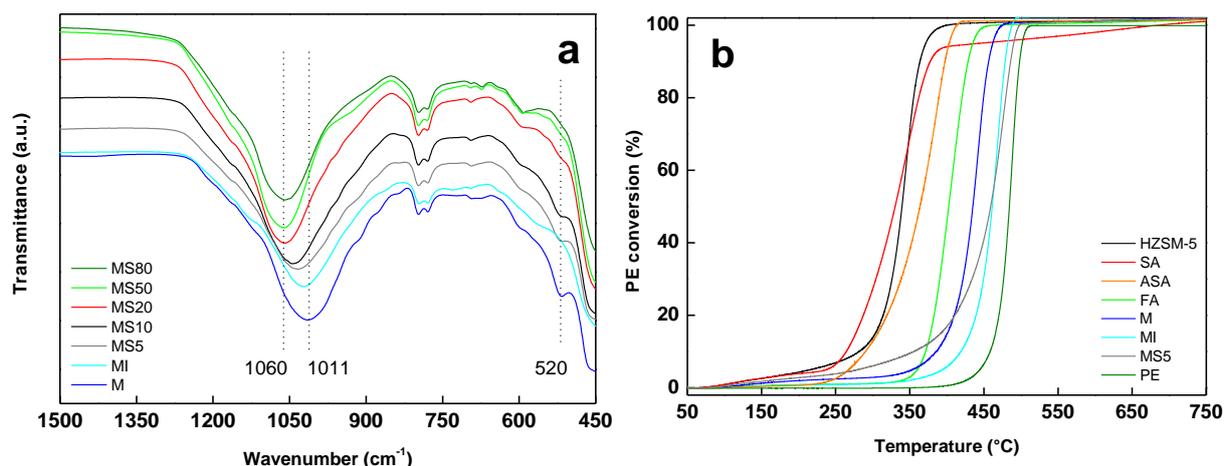


Figure 1. a) FTIR spectra of natural aluminosilicates treated with different concentrations of H₂SO₄ and b) PE depolymerization activity.

Results of PE depolymerization show that at temperatures above 450 °C thermal cracking is enhanced, because it does not suffer from mass transport limitations; on the other hand, at lower temperatures the catalyst role dominates. Observed activity in PE

depolymerisation (Figure 1b) generally correlates with the abundance of surface acid 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 resulted in improved catalytic performance at lower temperatures; compared to M sample, inferior activity was measured at higher temperatures, which is due to a considerable loss of tetrahedrally 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 [4]. For this reason, the activity of MAI and ASA catalysts was higher in comparison to M solid (see T_{50} values in Table 1).

Gas phase evolved during PE depolymerization was continuously monitored by means of on-line FTIR spectroscopy to identify the products; alkanes and alkenes were formed, the presence of aromatics could not be confirmed. In principle, isomerization occurred as well, resulting in a wide distribution of alkene structures. Over the M catalyst, exclusively alkanes with chain length up to 21 C atoms were present in the condensed liquid phase (53 % yield). Coke yield was very low (0.4 wt. %), while lower C2-C4 alkenes and alkanes constituted the remaining part.

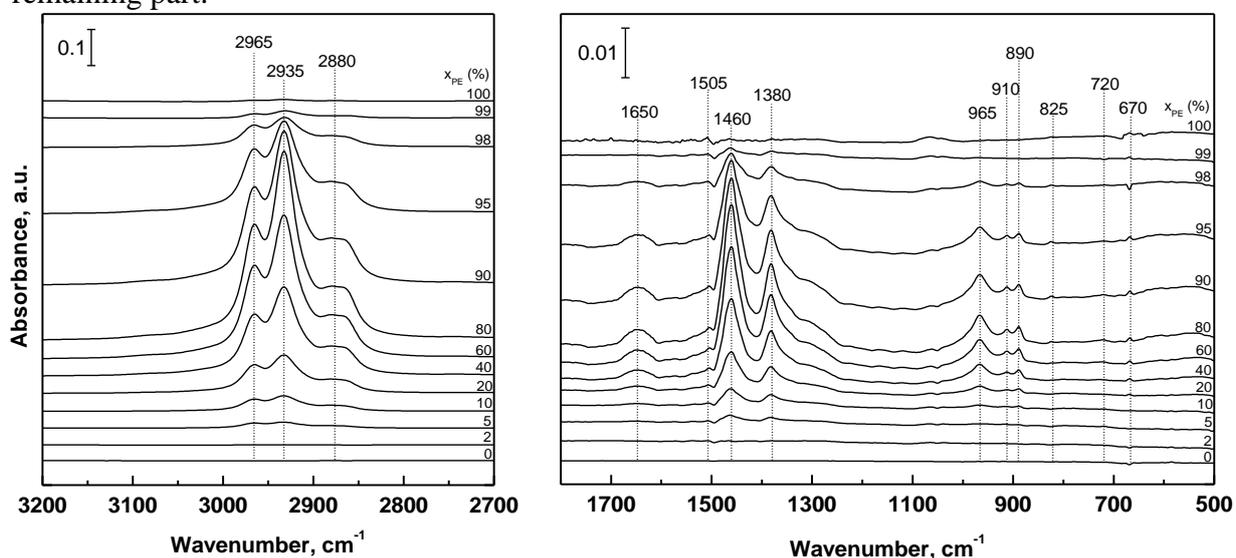


Figure 2. FTIR analysis of gas phase produced during PE depolymerization at different conversions using MAI catalyst.

For illustration, results of on-line FTIR spectroscopy of gaseous products obtained in the presence of Mal sample, are presented in Figure 2. Formation of alkenes can be confirmed from the absorption band at 1640-1650 cm^{-1} , belonging to symmetric stretching of C=C bond and C-H absorption band frequencies extending to wavenumbers higher than 3000 cm^{-1} . Additional information about the structure of produced alkenes can be obtained from bands in the 600-1000 cm^{-1} range. The ones at 990 and 910 cm^{-1} are indicative of vinyl group, while the band at 890 cm^{-1} shows the presence of vinylidene group. Bands at 965 and 690 cm^{-1} can be attributed to *trans*-di substituted and *cis*-disubstituted alkenes. The appearance of these bands shows that isomerization reaction occur during the PE depolymerization reaction, resulting in a wide distribution of alkene structures. Alkanes as main PE depolymerization products can be identified through intensive C-H absorptions in the 2860-2960 cm^{-1} range. Alkanes formed through scission of C-C bonds of the parent PE macromolecule comprise of methylene groups and terminal methyl groups, with the additional possibility of branched alkanes also being formed through isomerization reactions. The presence of terminal methyl group is confirmed by the absorption band at 1380 cm^{-1} . The band at 1460-1470 cm^{-1} can originate from asymmetric stretching of either methylene or methyl group. The band at 720 cm^{-1} originates from rocking of methylene groups. This band is more intense for

hydrocarbons having a longer C-C chain length. Intensity of bands at 720 and 1380 cm^{-1} reveals additional information on the carbon chain length. In alkanes with a very long chain (PE prior to depolymerization), the band at 1380 cm^{-1} is practically non-discernible, whereas this band becomes more obvious upon C-C bond cleavage in depolymerization products.

The pyrolysis kinetics of pure PE and physical mixtures of PE and catalysts (mass ratio 1:1) were determined from series of TGA experiments carried out at heating rates of 5-25 $^{\circ}\text{C}/\text{min}$. Prior to the numerical analysis, the TGA curves for PE were extracted from TGA curves recorded during pyrolysis of physical mixtures of PE and various catalysts. By means of integral

isoconversional analysis using Kissinger-Akahira-Sunose approach, the distribution functions for activation energy and frequency factors for various reaction models were determined from the filtered TGA data. A model evaluation was made by comparing the sum of normalized differences between isoconversional times of the PE TGA curves extracted from the experimental data and isoconversional times of calculated profiles, which were prior to analysis centrally aligned on the reaction time corresponding to the 50 % PE conversion. For the evaluation region a time frame bounded by 5 and 95 % PE conversions was used. Results confirmed that pyrolysis of pure PE and PE in the mixture with M sample follows the contracting sphere reaction model, while in the presence of MAI solid the PE pyrolysis could be well described by zero order reaction model. In the presence of ASA sample, PE decomposes according to the first order reaction model. In Fig.3 a comparison between calculated TG profiles of various reaction models and extracted PE TGA curve from TGA experiments carried out with the M sample at the heating rate of $\beta=10$ $^{\circ}\text{C}/\text{min}$ is shown.

CONCLUSION

The results of this study demonstrate that the natural aluminosilicates exhibit moderate activity for PE depolymerization. Acid leaching and Al grafting significantly increased the concentration of acid sites. Mesoporosity and Brønsted acidity enable high PE depolymerization activity. Negligible coking was obtained over the M catalyst; alkanes constitute the liquid phase, whereas alkenes are only present in the gas phase. The non-catalyzed PE pyrolysis and PE depolymerization carried out in the presence of various catalysts were well described by applying either the contracting sphere reaction model, or zero and first order reaction kinetics.

REFERENCES

- [1] L. Lloyd, *Handbook of Industrial Catalysts*, Springer, New York, 2011.
- [2] A. De Stefanis, P. Cafarelli, F. Gallese, E. Borsella, A. Nana, and G. Perez, *J. Anal. Appl. Pyrolysis*, 2013, **104**, 479-484.
- [3] G. Wu, W. Wu, X. Wang, W. Zan, W. Wang, and C. Li, *Micropor. Mesopor. Mater.*, 2013, **180**, 187-195.
- [4] P. Djinović, T. Tomše, J. Grdadolnik, Š. Božič, B. Erjavec, M. Zabilskiy, and A. Pintar, *Catal. Today*, 2015, **258**, 648-659.

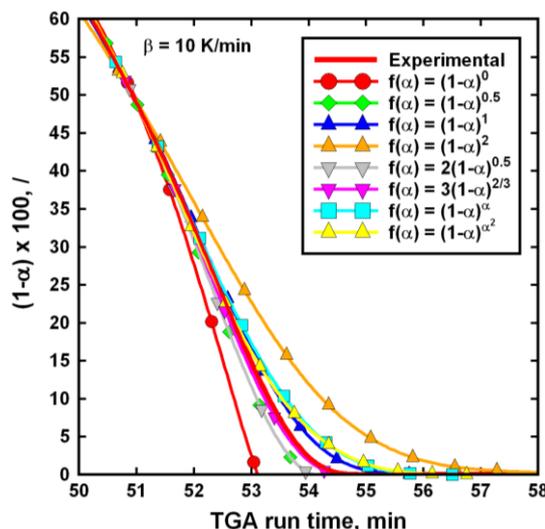


Figure 3. Comparison between PE TGA curves obtained for PE pyrolysis from PE/M mixture and curves predicted by various reaction models. Note: α stands for degree of PE conversion.