Studies of Zeolite-based Catalysts for Upcycling of Polymer Waste by use of PAL Spectroscopy

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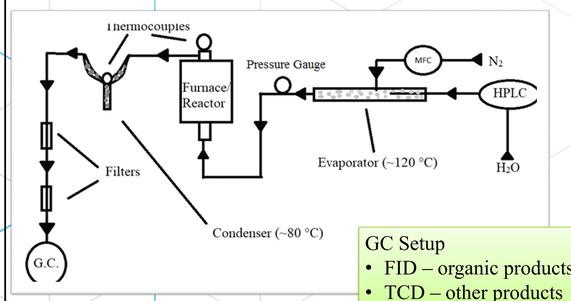
Purpose: *most efforts in plastic upcycling have focused on polyolefins justified by their high volume, but other high-volume polymers such as polyols and polyurethanes—those incorporating oxygen, exemplified by polyether polyols building blocks—are essential targets too. Polyols are overlooked plastics, although the ZSM-5 has been shown to convert polyols (among them polypropylene) into propionaldehyde with a selectivity of up to 90% {1}. Current studies show how polypropylene used in combination with ZSM-5 catalyst is affecting the catalyst during conversion process. The results suggest that* ***ZSM-5 treated with polypropylene does not alter its morphology as rapidly as treated with polyurethane****, which is remarkable since it allows using the catalysts several times before it is completely spent.*

In this studies the PAL was utilized to provide in depth information about catalysts nano- and meso-porous structure-changes during the conversion process. There were two series of measurements. Originally three different catalytic materials were used: "ZSM-5 pure", "ZSM-5 reacted with polyurethane" and "ZSM-5 reacted with polypropylene glycol", all processed one time through the reaction. In second series "ZSM-5 reacted with polypropylene glycol five times" was also investigated.

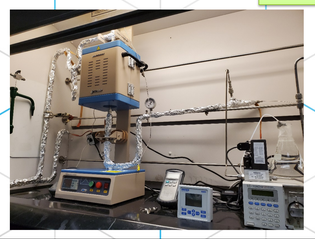
A catalytic process *was conducted in a* ***fluidized bed reactor*** *with a catalyst comprised of a zeolite with modifiers and metals at the University of South Carolina [2]. The recovered catalysts were pelletized and measured by use of TechnoAP spectrometer in short/long timing ranges [3] and analyzed by Kansy program [4].*

Fig.1 Overall Conversion Process in South Carolina University

Overall Process

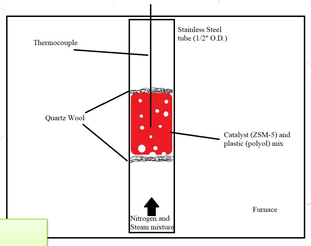


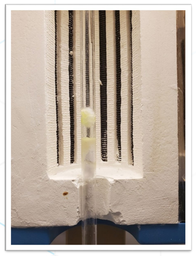
GC Setup
- FID – organic products
- TCD – other products



Reaction Conditions:
- Temperature: 250 °C
- Pressure: atmospheric
- Flow: 20 mL/min of N_2
  4.7 mL/min of Steam
- Zeolite Mass: 1.00 g
- Polyol Mass: 0.50 g

Reaction Conditions and Materials





Zeolite:
- Non-calcined ZSM-5 (NH_4-ZSM-5)
- Silicon to Aluminum Ratio: 50:1

Polyol:
- Polypropylene Glycol Mn 425

PAL results in Table 1 below are clearly "specimen specific". Trapping and o-Ps pick values are consistent with the literature values for ZMS-5 "pure" specimen. According to Table 2 the rates of changes are at or above 10% after treatment with polyurethane. PAL values for ZSM-5 treated with polypropylene glycol do not change much after one run. After the first treatment with popypropylene g. trapping lifetime, T_2 was ~ 491 ps, and o-Ps T_3=2.560 ns, with intensity at 8.7%; all these changes except the product of T_3 and I_3, which is a cumulative effect were less than 10%. Obviously five runs caused more changes [Fig.2]. **Still the morphological alteration, which is expressed by changes in trapping and positronium lifetimes & intensities after five runs with polypropylene glycol was less pronounced than after one run with polyurethane.**

sample	T1	I1	T2	I2	T3	I3	T3*I3
ZSM-5	0.155(0.004)	28.20(3.01)	0.496(0.016)	62.2006.67)	2.704(0.024)	9.597(0.698)	25.953
ZSM-5*1r polyurethane	0.159(0.004)	31.77(1.34)	0.449(0.010)	54.48(1.47)	2.179(0.091)	13.743(0.136)	29.947
ZSM-5*1r polypropylene g.	0.166(0.007)	29.20(1.43)	0.491(0.005)	62.08(0.81)	2.560(0.035)	8.717(0.612)	22.315
ZSM-5*5r polypropylene g.	0.167(0.006)	34.10(2.93)	0.450(0.002)	58.84(2.66)	2.329(0.016)	7.060(0.269)	16.439

Table.1: PAL average results for four different specimens measured during series 1-2, with source correction.

sample	T1	I1	T2	I2	T3	I3	T3*I3
ZSM-5 reference	0.155	28.203	0.496	62.200	2.704	9.597	25.953
ZSM-5*1 polyurethane	2.6%	12.7%	-9.6%	-12.4%	-19.4%	43.2%	15.4%
ZSM-5*1 polypropylene	6.9%	3.5%	-1.1%	-0.2%	-5.3%	-9.2%	-14.0%
ZSM-5*5 polypropylene	7.2%	20.9%	-9.4%	-5.4%	-13.9%	-26.4%	-36.7%

Table.2: Relative change in PAL values as compared to ZSM-5 used as reference

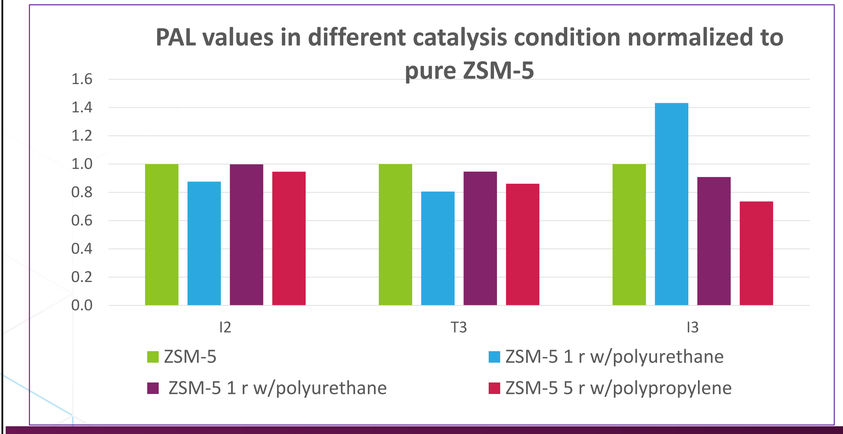


Fig.2: : PAL results after source correction normalized to ZSM-5, for I2, T3 and I3

PAS data indicate that polypropylene is a better material for plastic conversion since it does not alter the catalyst that much like polyurethane. According to the PAL data morphological alteration of ZSM-5 catalyst treated with polypropylene five times is less significant than the alteration in ZSM-5 treated with polyurethane just for one time.

References

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