Improving oil quality from waste plastics pyrolysis: aromatization and dehalogenation activity using MFI zeolites

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Introduction and Motivations

The shift to a circular economy has heightened the focus on energy and carbon efficiency, making plastics recycling essential due to their energy-intensive production, widespread use, and environmental persistence. Chemical recycling, especially pyrolysis, is gaining attention for converting plastic waste into petrochemical feedstocks like olefins and aromatics. In this way, pyrolysis thermally decomposes plastics into valuable products but faces challenges from feedstock contamination and quality issues. In particular, the presence of halogenated species (mostly Cl-containing compounds) strongly limits the possible upgrading of the waste plastics pyrolysis oil in refinery units. Zeolites, particularly ZSM-5 (MFI), have emerged as highly effective catalysts in post-pyrolysis treatments to address these issues. ZSM-5 is known for its unique microporous structure and acidity, which enhance oil quality by increasing light hydrocarbon yields, reducing impurities such as halogens, and optimizing the hydrocarbon composition.[1] In this context, this study aims to improve the quality of an oil obtained from the pyrolysis of real waste plastics by exploring how the synthesis method and the properties of ZSM-5 zeolite affect the efficiency of the dehalogenation process and the generation of aromatic compounds in the treated oil.

Materials and Methods

The feedstock oil was characterized using various analytical techniques[1]. This oil exhibits a notably high chlorine concentration (290 ppm) and is predominantly enriched with aliphatic compounds, particularly paraffins, whereas the content of aromatic hydrocarbons is small (c.a. 5.5 wt%). Additionally, it contains a significant fraction of heavy compounds, comprising 43.5 wt%, which are undetectable by GC-MS. A ¾" diameter fixed-bed reactor was used for the oil upgrading catalytic tests, with the oil being fed through an HPLC pump. Four ZSM-5 zeolite samples were tested at 450 °C and a WHSV of 5 h^{-1}. These included one microcrystalline and three nanocrystalline zeolites, each synthesized using distinct methods (Table 1): *nano 1* by milling the microcrystalline zeolite, *nano 2* from an amorphous aluminosilicate hydrogel made with fumed SiO_2 and sodium aluminate, using buthylmethylpyrrolidinium hydroxide (BMC5) as the organic structure-directing agent (OSDA), and *nano 3* through hydrothermal conversion of FAU, also employing BMC5 as OSDA[2]. At the reactor outlet, a condensation system allowed liquid samples to be taken at different reaction times, which were analyzed using the same techniques as the feedstock oil. The gases were collected with the help of a totalizer, and their composition was determined using μ-GC.

Table 1. Characterization of the feedstock oil and zeolite samples. [1]: CHNS-O, [2]: AOD-IC, [3]: GC-MS, [4]:ICP-MC, [5]: N_2 adsorption (77 K).

Oil elemental composition (wt%)		Raw oil molecular composition (wt%)[3]		Zeolite characterization					
				Sample	Si/Al[4]	S_{BET} (m^2/g)[5]	S_{Ext} (m^2/g)[5]	V_{mic} (cm^3/g)[5]	V_{total} (cm^3/g)[5]
C[1]	85.52	Mono-aromatics (MAH)	5.5	ZSM-5 (micro)	13.9	431	36	0.16	0.22
		Naphthenes (NAPH)	7.2	ZSM-5 (nano 1)	14.0	415	87	0.14	0.33
H[1]	14.45	Olefins (OL)	8.2	ZSM-5 (nano 2)	38.6	363	115	0.15	0.16
Cl[2]	0.029	Paraffins (PAR)	35.6	ZSM-5 (nano 3)	39.4	385	170	0.16	0.16

Results and Discussion

Figure 1 summarizes the key results of oil upgrading experiments conducted with various zeolites. The data indicate that zeolites synthesized using BMC5 as OSDA (nano 2 and nano 3) exhibit no significant differences in performance. However, a notable distinction arises when comparing ZSM-5 (micro) with its milled counterpart (ZSM-5 nano 1). Milling the ZSM-5 zeolite substantially reduces gas yield from 15.7 wt% to 6.7 wt%, reflecting a diminished cracking capacity. This reduction can be attributed to a decrease in Brønsted acidity caused by the milling process (0.9 and 0.52 mmol/g for micro and nano1, respectively).

All tested zeolites demonstrated significant activity in aromatization reactions, particularly noteworthy given the initial aromatics content of 5.5 wt% in the feed oil. The differences in performance were relatively modest in spite of the great variations observed between the zeolite properties. It can be envisaged that the lower Al content of samples ZSM-5 (nano 2) and ZSM-5 (nano 3) is compensated by their enhanced accessibility due to their larger surface area. Thus, the highest yield of aromatics, 15.1 wt%, was achieved with ZSM-5 (nano 2).

Another noteworthy parameter is the chlorine concentration in the upgraded oil and how it evolves as a function of time on stream (Figure 1c). Also, in this case, zeolites ZSM-5 (nano 2) and ZSM-5 (nano 3) exhibit greater dehalogenation efficiency and a better stability showing lower deactivation along the time on stream. Among these, ZSM-5 (nano 3) achieves the lowest chlorine concentration (40 ppm at 0.5 h). Conversely, ZSM-5 (micro) and ZSM-5 (nano 1) zeolites demonstrate a lower dehalogenation capacity, with a fast increase in the oil Cl content along the time on stream. Therefore, regarding the oil dehalogenation process, the zeolite accessibility also plays a more relevant role than the Al content.

Based on these findings, it can be concluded that ZSM-5 zeolites are highly promising materials for improving the quality of waste plastics pyrolysis oil, making them suitable candidates for the development of pre-treatment processes before injecting the upgraded oils into existing refinery units.

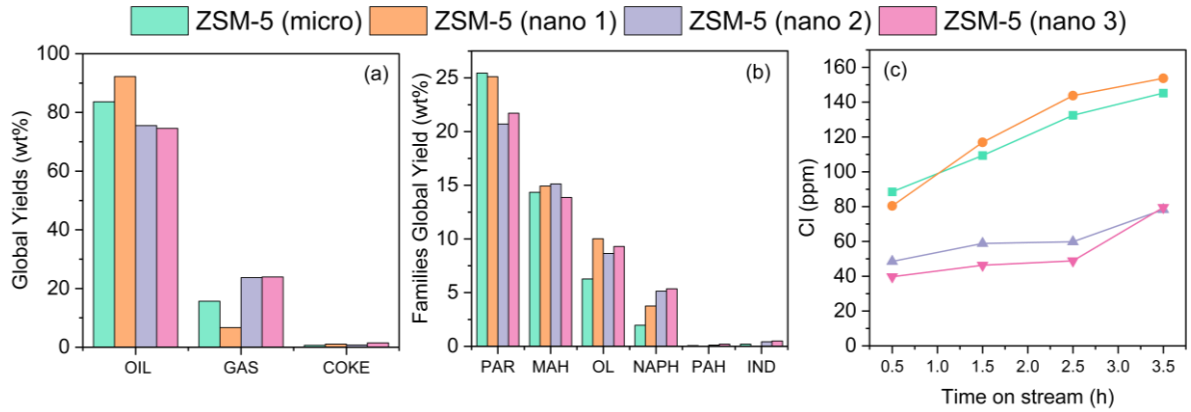

Figure 1. (a) Global mass yields of the different fractions, (b) global yield of the main families obtained in the oil, (c) Cl concentration in the oil as a function of the reaction time on stream.

References

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