

Selective light olefin production from PVC-contaminated plastic waste through catalytic pyrolysis: effect of phosphorous modification and mesopore introduction

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Highlights

- Light olefin selectivity of 80% was achieved.
- Phosphorous impregnation improved catalyst stability against dealumination.
- PVC contamination in feed caused faster catalyst deactivation.

1. Introduction

Recycling polyolefins is vital for achieving sustainability goals in the chemical industry and advancing a circular economy. In recent years, chemical recycling methods such as pyrolysis have garnered attention for their ability to convert plastic waste into valuable products thermochemically. Catalytic pyrolysis has emerged as a promising route. This approach reduces energy requirements and enhances selectivity for valuable products, like light olefins (C₂-C₄ olefins), essential platform chemicals for various plastic products and chemicals [1]. However, hazardous contaminants in plastic waste, such as polyvinyl chloride (PVC), pose a significant threat to catalytic pyrolysis. PVC pyrolysis forms highly corrosive and poisonous HCl gas, severely and irreversibly deactivates the catalyst by causing dealumination and rupturing the catalyst framework. Polypropylene (PP) finds widespread use in packaging, construction materials, and medical equipment, resulting in PP waste with varying compositions and PVC contamination levels, thereby limiting its recycling rate. Catalytic pyrolysis of PP waste demands a robust catalyst that can selectively convert different polyolefins to light olefins while preserving its performance. Considering these challenges, this research focuses on the effect of phosphorus impregnation and mesopore introduction on catalyst stability and light olefin selectivity. Thus, catalytic upgrading of PVC (5 wt.%) containing PP pyrolysis vapors was investigated using the micro-pyrolyzer facility combined with comprehensive two-dimensional gas chromatography (GCxGC-FID/TOF-MS). This analytical approach enables accurate quantification and identification of complex pyrograms, shedding light on the intricate process of pyrolysis and catalyst performance, further supported by determining changes in surface characteristics of post- and pre-pyrolysis catalysts through X-ray photoelectron spectroscopy (XPS).

2. Methods

Catalyst properties were investigated via temperature-programmed desorption of NH₃, N₂ physisorption, and XPS analysis. Details about the synthesis of P-modified HZSM-5 (P-HZSM-5) and P-modified mesoporous HZSM-5 (P-mesoHZSM-5) can be found elsewhere [1, 2]. The pyrolysis and catalytic reactors were maintained at 550 °C and 600 °C. The catalyst to plastic (C/P) ratio was kept at 80 (wt./wt.) for modified catalysts and 20 (wt./wt.) for the parent HZSM-5 due to its significantly higher acidity.

3. Results and discussion

HZSM-5, P-HZSM-5, and P-mesoHZSM-5 exhibited acidity levels of 0.65, 0.1, and 0.09 mmol NH₃/g, respectively. This reduction in acidity, due to steaming and catalyst modifications, slightly decreased the light olefin yields obtained with fresh catalysts when pure PP was used as the pyrolysis feedstock. However, it improved the stability against coke deposition. For instance, HZSM-5 exhibited a light olefin selectivity of 79 wt.% in the first experimental run, whereas modified catalysts yielded 75 wt.% light olefins. However, over the course of 150 consecutive experiments, the parent HZSM-5 suffered from the most severe activity loss, with light olefin selectivity decreasing to 43 wt.%. P-HZSM-5 and P-mesoHZSM-5 preserved their activity to a greater extent, yielding 57 and 63 wt.% light olefins,

respectively. Importantly, deactivation was reversible, with all the catalysts yielding similar results to their fresh counterparts after regeneration through coke combustion with air at 700 °C. When PP was deliberately contaminated with 5 wt.% of PVC, the light olefin yields were improved slightly by 4 wt.% for parent HZSM-5 and P-mesoHZSM-5. Interestingly, this improvement was not observed for P-HZSM-5, which could be attributed to mass transfer limitations imposed by the already-narrowed micropores due to phosphorus deposits. These limitations might compensate for the synergistic effect of PP-PVC co-pyrolysis on light olefin selectivity. Moreover, activity reduction occurred relatively faster than the catalytic pyrolysis using pure PP as feedstock, with the light olefin selectivity of the catalysts decreasing to below 65 wt.% in 50 runs. The catalyst regeneration results revealed further insights. While modified catalysts successfully yielded similar light olefins to their fresh counterparts, activity loss of HZSM-5 was permanent, yielding only 60 wt.% light olefins. This was due to the dealumination caused by the HCl, which severely damaged the catalyst framework and reduced its acidity. However, phosphorus impregnation helped the modified catalyst preserve alumina in the catalyst matrix (**Figure 1B**), thus maintaining its activity. Furthermore, the observed decrease in the Si/Al ratio in the modified catalysts (see **Figure 1**) indicates that phosphorus deposits on the catalyst surfaces interacted with the leached alumina migrating from deeper sections of the matrix, most likely forming silicoaluminophosphate (SAPO) species on the surface which are known to be active for olefin cracking.

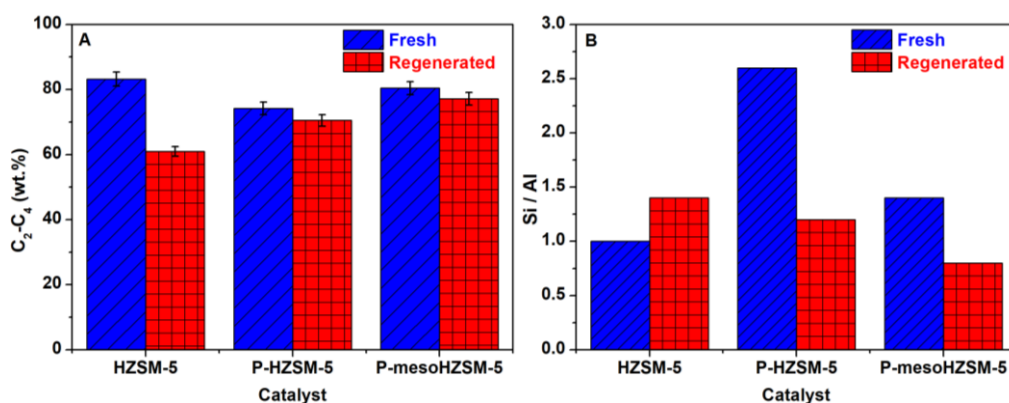


Figure 1. Light olefins (C₂-C₄) yields obtained with fresh and regenerated catalysts (A). Si/Al ratio of fresh and regenerated catalysts obtained with XPS (B).

4. Conclusions

Polypropylene was effectively converted into light olefins with high selectivity using parent, P-modified, and mesoporous P-modified HZSM-5 catalysts. P-impregnation with mesopore introduction enhanced light olefin selectivity and stability against coke formation during polypropylene pyrolysis. Deactivation due to coke formation during pure PP pyrolysis vapor cracking over 150 runs was reversible, as all the catalysts were successfully regenerated. Pyrolysis of PVC-contaminated PP led to even faster deactivation for all catalysts, with light olefin selectivity dropping to below ~65 wt.% even after 50 runs. However, the P-modified catalysts were effectively regenerated, whereas the parent HZSM-5 exhibited permanent activity loss. P-modification prevented dislodged alumina from leaving the zeolite framework by interacting with Si and leached Al to form SAPO species, thereby preserving the framework and acidity. Considering the significant impact of 5 wt.% PVC contamination in the feed, the development of robust catalysts is essential for scaling up the proposed plastic waste recycling route, where P-impregnation has demonstrated promising results.

References

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Keywords

Polyvinyl Chloride, Exsitu pyrolysis, Catalyst deactivation, Light olefins.