Pyrolysis-Catalytic Reforming of Brominated High Impact Polystyrene over Fe- and Ni-Modified ZSM-5 Catalysts

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Abstract The pyrolysis-catalytic reforming experiments of Brominated High Impact Polystyrene (Br-HIPS) were performed by a two-stage fixed bed reactor in the presence of Fe- and Ni- modified ZSM-5 catalysts, with the aim of investigating the product distribution and debromination performance in relation to different catalysts. The characterizations of the catalysts and reacted catalysts were performed by BET, XRD, SEM and NH_3-TPD. The results showed that the Fe- and Ni- modified catalysts decreased the BET surface areas and pore sizes of HZSM-5, while the total acidity of Ni/ZSM-5 increased. In the absence of a catalyst, Br-HIPS plastic produced a maximum liquid yield of 81.6 wt%, including the oil and wax products. The addition of HZSM-5 reduced the yield of oil from 69.0 wt% to 64.4 wt%, with an increase of gas products from 7.7 wt% to 14.3 wt%. Furthermore, the modified catalysts of Fe/ZSM-5 and Ni/ZSM-5 exhibited more intense catalytic cracking performance, which decreased the yield of oil into 63.2 and 61.2 wt%, respectively. In terms of the composition in the pyrolysis oils, it was found that more sing ring aromatics obtained in the presence of Fe/ZSM-5 catalyst, while the addition of Fe/ZSM-5 and Ni/ZSM-5 catalysts promoted more two-ring aromatics produced in the expense of sing ring aromatics. In addition, the results indicated that the modified catalysts were found to be very effective at removing bromine in the pyrolysis oil. The Fe/ZSM-5 catalyst intended to capture more inorganic bromine and the Ni/ZSM-5 catalyst might be more favor of organobromine compounds cracking. Thus this work could provide an efficient approach for reusing these pyrolysis oils.

1. Introduction

Electronic waste plastics (e-waste plastics) have been one of the emerging and fastest-growing waste streams due to the increasing number of generation in waste electrical and electronic equipment (WEEE) (Baldé *et al*, 2015). Given that brominated flame retardant (BFR) materials in e-waste plastics have been the major impediment for recycling treatment, chemical recycling has been proposed as an environmentally friendly method of recycling e-waste plastics for clean fuels production or chemical feedstocks (Grause *et al*, 2011; Ma *et al*, 2016a). For the sake of hazardous plastic waste, advanced handling methods are essential to eliminating the toxic flame retardant additives for the feedstock recycling of WEEE plastics. Thus, researchers have been trying to improve the feedstock recycling process with the aim of generating high quality bromine-free chemicals and alternative fuel-like products (Yang *et al*, 2013; Ma *et al*, 2016b; Ma *et al*, 2017).

Br-HIPS, which approximately accounts for 25 wt% of all WEEE plastics, contains high concentration of polybrominated diphenyl ethers (PBDE) and Sb_2O_3 additives (Ma *et al*, 2017), has been the main subject for pyrolysis studies in recent years. Compared to the thermal degradation, catalytic degradation of plastics requires a lower temperature. More importantly, the shape selectivity exhibited by certain catalysts degradation could yield high-quality liquid and higher value products or even bromine-free chemicals (Ma *et al*, 2016a; Yang *et al*, 2013). In our previous paper, it was found that the product distribution and debromination performance had interrelationship with the properties of catalysts, including textural and acidic property. However, there is still a long way to go for the feedstock recycling of flame retarded plastics (Ma *et a*l, 2017). Thus, the pyrolysis-catalytic reforming process is promoted, which is a two-step process that involves the pyrolysis of BFR-plastics and catalytic up grading of the pyrolysis products.

In this paper, the pyrolysis-catalytic reforming experiments of Br-HIPS were performed in a two-stage fixed bed reactor at a final pyrolysis temperature of 450 °C, with the aim of investigating the product distribution and debromination performance the presence of different modified catalysts. Meanwhile, the effect of the catalysts on the migration and transformation behaviors of bromine existing in the pyrolysis products was demonstrated for enhancing the potential benefits of feedstock recycling for high quality bromine-free fuel oils.

2. Results and Discussion

The product yields from pyrolysis-catalytic reforming experiments of Br-HIPS over the catalysts were showed in Fig. 1. With the addition of quartz, the majority of the pyrolysis products derived from Br-HIPS were oil and wax accounted for 81.6 wt%, with 10.4 wt % char and 7.7 wt % gas, indicating the fact that the liquid products were the main fraction during the pyrolysis. It was also found that 0.14 wt% of coke was obtained in the quartz. In the presence of HZSM-5 catalyst, the yield of oil reduced from 69.0 wt% to 64.4 wt%, with an increase of gas products from 7.7 wt% to 14.3 wt%. Furthermore, the modified catalysts of Fe/ZSM-5 and Ni/ZSM-5 exhibited more intense catalytic cracking performance, which decreased the yield of oil into 63.2 and 61.2 wt%, meanwhile, the yield of gas increased to 16.1 and 20.3 wt%, respectively. On the other hand, it was

found that the coke produced in the modified catalysts was increased compared to HZSM-5 zeolite. The results indicated that the modified catalysts exhibited more remarkable cracking performance, especially the Ni/ZSM-5 catalyst, which due to its high acidity and porosity of catalyst.

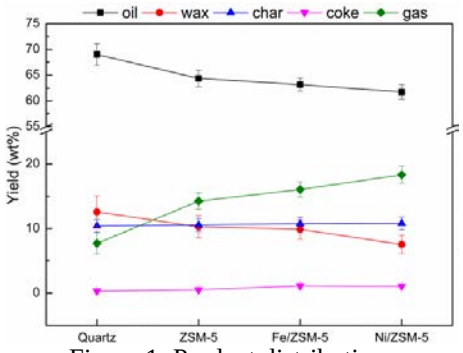

Figure 1: Product distribution

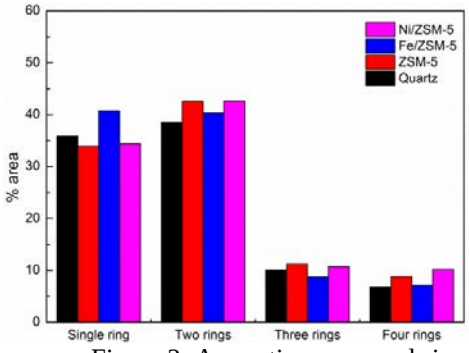

Figure 2: Aromatic compounds in oils

The pyrolysis oils were further characterized using GC-MS and the percentages of the single ring to four ring aromatic compounds determined by the peak area are presented in Fig. 2. The main pyrolysis products were toluene, ethylbenzene, styrene, cumene, 1,3-diphenylpropane and 1,3-diphenylbutane and so on, and most of these compounds are valuable chemical feedstocks. It was found that the sing ring aromatics decreased in the presence of ZSM-5 catalyst and Ni/ZSM-5 catalysts, simultaneously promoting more two-ring aromatics produced. It may be attributed to the fact that two competing reactions took place for the polymer cracking, and the presence of ZSM-5 and Ni/ZSM-5 catalysts could promote the cross-linking reactions occurred due to their high acidity and porosity. While the addition of Fe/ZSM-5 increased sing ring aromatics to 43%, especially increased the concentration of styrene. It could be attributed to the fact the loading of active Fe_2O_3 may lead to the β-scission reaction rather than hydrogen transfer via carbanion mechanism, which played a key role on the production of aromatic olefins. On the other hand, the multi-ring aromatic compounds significantly increased. It could be related that the decrease yield of wax may lead more relative light aromatic compounds transfer into the oil, which may result in the increase of multi-ring aromatic compounds in oils. It was also proposed that the formation of multi-ring aromatic compounds in the pyrolysis oil was attributed to the Diels-Alder reaction

Furthermore, the bromine content of the pyrolysis oil was determined by the EPA method 5050. The results showed that the bromine in the plastic was mainly enriched in the oil and wax. The presence of ZSM-5 catalyst reduced the bromine content from 8.67 wt% to 5.7 wt%. when the Fe/ZSM-5 and Ni/ZSM-5 were used, the bromine content in the oils decreased to 0.7 wt% and 0.6 wt%, respectively. It indicated that after the iron oxide loading, the debromination performance of Fe/ZSM-5 improved, which was possibly attributed to the capture of inorganic bromine derived from the Br-HIPS pyrolysis and fixed on the catalyst. However, the sound debromination performance of Ni/ZSM-5 catalyst could due to its high acidity and porosity, which could promote more organobromine compounds further cracking into inorganic bromine.

3. Conclusion

The pyrolysis-catalytic reforming experiments of Br-HIPS were performed by a two-stage fixed bed reactor in the presence of modified ZSM-5 catalysts. The results showed that the addition of HZSM-5, Fe/ZSM-5 and Ni/ZSM-5 reduced the yield of oil from 69.0 wt% to 64.4, 63.2 and 61.2 wt%, respectively. In terms of the composition in the pyrolysis oil, it was found that more sing ring aromatics obtained in the presence of Fe/ZSM-5 catalyst, while the addition of Fe/ZSM-5 and Ni/ZSM-5 catalysts promoted more two-ring aromatics produced in the expense of sing ring aromatics. In addition, the results indicated that the modified catalysts were found to be very effective at removing bromine in the pyrolysis oil. The Fe/ZSM-5 catalyst intended to capture more inorganic bromine and the Ni/ZSM-5 catalyst might be more favor of organobromine compounds cracking.

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