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Full Length Article

Influence of Fe based ZSM-5 catalysts on the vapor intermediates from the pyrolysis of brominated acrylonitrile-butadiene-styrene copolymer (Br-ABS)

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ABSTRACT

The catalytic upgrading of the vapor intermediates from the pyrolysis of brominated acrylonitrile-butadiene-styrene (Br-ABS) was investigated over the Fe/ZSM-5 catalysts in a two-stage fixed bed reactor. Results showed that HZSM-5 and Fe/ZSM-5 catalysts exhibited high catalytic cracking activities, resulting in the increased yield of oil from 62.8 wt% to 64.3 wt% and 66.7 wt%, respectively. When the higher amounts of Fe/ZSM-5 catalysts were applied, the oil yield decreased to 59–61.6 wt%, whereas high amounts of coke were deposited on the catalysts. On the other hand, the higher percentages of the single ring and 2 ring aromatic compounds in the oils was obtained by the Fe/ZSM-5 catalysts, compared to the thermal pyrolysis and the catalytic upgrading by the parent HZSM-5 catalyst. The Fe/ZSM-5 catalysts significantly promoted the formation of styrene monomer and dimer derivatives. It could be proposed that the Fe based materials was in favor of the depolymerization of the polymer matrix, providing the styrene sources for the secondary oligomerization over the parent HZSM-5 catalyst. In addition, the Fe/ZSM-5 catalyst exhibited effective debromination performance, by means of cracking the organobromine compounds and capturing the inorganic bromine in the catalyst. The possible catalytic cracking mechanism over the Fe/ZSM-5 catalyst was discussed.

1. Introduction

It is estimated that the global production of e-waste reached up to approximately 48 million tons in 2014 with an annual growth rate of 5% [1]. In general, approximately 30% of the total e-waste consists of plastics, among which acrylonitrile-butadiene-styrene (ABS) and high-impact polystyrene (HIPS) plastics make up a significant proportion of 55% [2]. However, most of the plastics generally include brominated flame retardants (BFRs) and the synergists Sb_2O_3 for the fire safety performance of polymer materials, which has caused serious threats to the environment and human health after improper disposal [3].

Currently, the main process routes for plastic waste management are 39.5% used for energy recovery, 30.8% disposed to landfill and only 29.7% recycling [4]. Instead of landfilling or incineration, alternative methods of thermochemical recycling aimed to convert waste plastics into fuels and chemicals have been proposed as promising technologies for environmentally friendly utilization of waste plastics [5–7]. However, the unpleasant aspect of BFRs existed in plastics has been the major problems due to a large production of toxic brominated compounds during the feedstock recycling process.

Extensive studies have been investigated for the pyrolysis behavior of brominated HIPS (Br-HIPS) and brominated ABS (Br-ABS) [6–8]. It has been widely suggested that the pyrolysis of the brominated plastics includes two steps with the release of bromine at low temperature region and the decomposition of polymer matrixes at relative high temperature [8]. Consequently, the pyrolysis process of brominated plastics generated a large quantity of toxic brominated compounds, such as $SbBr_3$, HBr and organobromine compounds, which apparently hinder the reuse of these plastics [9–11]. For example, Hall and Williams investigated the pyrolysis of Br-HIPS in a fluidized bed reactor and over 90 wt% of pyrolysis oil was obtained with 98% of Br transferring into the oil [10]. Bhaskar et al. [11] studied the pyrolysis of Br-ABS in a fixed bed reactor and recovered 39 wt% of oil and 32 wt% of wax residue, whereas more than 78.8% of Br was detected in the wax products. Therefore, the simple pyrolysis could not make the recovered oil products satisfy the requirement of feedstocks due to the presence of brominated compounds in the liquid.

Recently, a wide range of catalysts has been utilized for the catalytic pyrolysis of brominated plastics, including metallic oxides [9,12–14], zeolites [15–18], fluid catalytic cracking (FCC) catalysts [19] and mesoporous materials [17,18], etc. It has been proved that zeolites can achieve a remarkable removal of bromine in the oil, while the catalysts greatly altered the yield of oil and the composition of the pyrolysis products [17–19]. The metallic oxides were applied for the catalytic

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pyrolysis of Br-ABS and the results showed that the primary degradation products were influenced by the composition and crystalline structure of different iron oxides [12,13]. Meanwhile, the addition of iron oxides exhibited fixation abilities of bromine and could effectively suppress the formation of HBr and organobromine compounds during the pyrolysis of tetrabromobisphenol A (TBBPA) [20,21]. However, the catalytic activities of catalysts have been another controversial issue due to the deactivation of catalyst caused by the coke formation in the single catalytic pyrolysis process.

In our previous work, a two-stage pyrolysis and catalytic upgrading of Br-HIPS was investigated [22]. The results showed that the Fe modified ZSM-5 and MCM-41 catalysts could promote their catalytic activities and debromination efficiency. Meanwhile, the two-stage process could greater control the temperature for each stage and minimize the sintering problems of catalysts. However, the Br-ABS plastic containing TBBPA flame retardant, accounting for 30 wt% of the brominated plastics, has scarcely been studied under the pyrolysis-catalytic upgrading process. Therefore, a thorough study of pyrolysis-catalytic upgrading process of Br-ABS was presented in this work. The work mainly includes: (1) the effect of Fe/ZSM-5 catalyst with different addition ratios on the product yield and the oil product composition, (2) the debromination performance of the catalyst was evaluated, and (3) the possible catalytic mechanism of the catalyst on the vapor-phase intermediates derived from Br-ABS pyrolysis was investigated.

The extensively study on the pyrolysis-catalytic upgrading process of brominated plastics will contribute to a better understanding of the pyrolysis and catalytic cracking performance of brominated plastics for bromine-free fuels and chemical feedstocks, providing the potential benefits of feedstock recycling of waste plastics.

2. Experimental

2.1. Materials

The brominated acrylonitrile-butadiene-styrene (Br-ABS) plastic (PA-765A) was supplied by Qimei Co., Ltd. Zhenjiang, China. The ABS was flame retarded with tetrabromobisphenol A (TBBPA) and synergist Sb_2O_3. The sample was pulverized under liquid nitrogen cooling system and sieved to the particle size < 0.6 mm. The proximate and ultimate analyses of Br-ABS are presented in Table 1. The HZSM-5 zeolite ($SiO_2/Al_2O_3 = 25.8$) was supplied by the catalyst factory of Nankai University in Tianjin, China. About 10 wt% of Fe loading on the HZSM-5 catalyst was prepared by wet impregnation method as described elsewhere [22]. The catalysts were characterized by different techniques and presented in Table 2. The details of the characterization of the catalysts have been illustrated previously [22].

2.2. Experiment procedures

The pyrolysis-catalytic upgrading experiments were performed in a two-stage fixed bed reactor, as detailed elsewhere [22]. The reaction system consisted of a quartz tube (total height: 660 mm) with two separate heating zones. The first stage was the pyrolysis zone with a height 200 mm, ID 40 mm, and the second stage was the catalytic upgrading zone with a height 200 mm, ID 30 mm. The pyrolysis of Br-ABS plastic (5 g) was undertaken in a quartz crucible at the first stage, heating the sample from ambient temperature to 450 °C at 10 °C min^{-1} and held for 60 min. The catalytic upgrading of the vapor products took place at the second stage with the catalyst (0.5 g) supported on quartz wool and previously heated to 450 °C. For comparison, the quartz sand was substituted for the catalyst during the pyrolysis of Br-ABS without catalyst. Furthermore, for the Fe/ZSM-5 catalyst, experiments with different weight ratios (Br-ABS/catalyst) of 5/0.5, 5/1 and 5/2 were carried out, and the corresponding catalysts were denoted as FZ-0.5 (0.5 g), FZ-1 (1 g) and FZ-2 (2 g) for simplicity. Nitrogen gas at the flow rate of 50 ml min^{-1} was used as the carrier gas. The volatile products exited from the reactor were captured by ice/salt bath condensers. The gas products of HBr or Br_2 during pyrolysis were trapped in an alkali solution ($Na_2CO_3/NaHCO_3$) flask. The uncondensed gases were collected in a gas sample bag.

The main products derived from the Br-ABS plastic pyrolysis consist of oil/wax, gas and char residue. The oil products were condensed in the tar trap while the mass of wax coated on the wall of the reactor. The separation of oil and wax was described in detail previously [18]. The char residue was determined by the weight different of the crucible before and after each experiment. The mass of gaseous products was obtained by the method of difference. The amount of coke deposition on the catalyst was calculated by the weight difference of the catalyst before and after each experiment.

Table 1
Proximate and ultimate analyses of Br-ABS.

Proximate analysis	wt%	Ultimate analysis[a]	wt%
Moisture	0.2	C	77.5
Volatile matter	98.2	H	7
Fixed carbon	0.3	N	2.8
Ash	1.3	O[b]	1.4
		Br	8.6
		Sb	2.7

[a] Dry and ash free basis.
[b] By difference.

2.3. Analytical methods

The ultimate and proximate analyses of the sample were respectively determined using an elemental analyzer (Vario Micro cube, Elementar Inc., Germany) and TGA-2000 (Las Navas Instruments, Spain). The bromine content of the sample and products was determined by the EPA method 5050. The antimony content of the sample and products was determined in a digestion system with a mixture solution of sulfuric and nitric acid and then analyzed using inductive coupled plasma-mass spectrometry (ICP-MS), as described previously [17].

The oil was diluted in chloroform (1:10 v/v) and analyzed by a gas chromatograph-mass spectrometer (GC/MS, Agilent 7890A/5975C) with a capillary column (HP-5MS, length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm). The column temperature was programmed from 40 °C (held for 5 min) to 300 °C at 10 °C min^{-1}, and then held for 10 min. The injector temperature was 280 °C. Compounds were identified using the National Institute of Standards and Technology (NIST) library with similarity indices of $> 90\%$, based on the matches of their retention times and MS spectra data for those standards. Quantification was carried out by the external standard methods and was calibrated with aromatic standards using the relative retention times once the component was reliably identified on GC/MS [17].

The spent catalysts were characterized by a powder X-ray diffraction (XRD) X'Pert PROX diffractometer with monochromatic Cu Ka radiation (PANalytical B.V., 40 kV and 40 mA). The XRD spectra were recorded in the 2θ range of 5–80° at a scanning rate of 12° min^{-1}. The coke deposition on the catalysts was analyzed using a thermogravimetric analyzer (PerkinElmer STA 8000). The spent catalyst (10 mg) was heated in an air atmosphere from the ambient temperature to 800 °C at a heating rate of 10 °C min^{-1}. The flow rate of air was 100 ml min^{-1}.

3. Results and discussion

3.1. Product yield

In this paper, the Br-ABS/catalyst with different weight ratios of 5/0.5, 5/1 and 5/2 were investigated to determine the influence of the