

Effect of HCl Pretreatment on the Performance of Natural Zeolite in a two-stage Pyrolysis and Catalytic Reforming of Polypropylene and Polystyrene

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This study investigated the performance of three kinds of natural zeolites (NZ) after HCl pretreatment in different concentration and one commercial zeolite catalyst (HY-zeolite) in a sequential pyrolysis and catalytic reforming of polypropylene and polystyrene. The natural zeolite was pretreated by 0.5, 1, 6 mole HCl solution under the reflux condition. The untreated natural zeolite and HY-zeolite were also used as catalyst in this experiment for comparison. The experiments were carried out on two stage reactor using semi-batch system, and implemented in the absence and presence of catalyst. The results show that the pretreatment in HCl solution could increase the surface area and the Si/Al ratio of natural zeolite. The pretreatment affected greatly on the component of liquid product when the concentration of the HCl solution was changed from 0.5 to 1 mole/L.

Key Words: HCl pretreatment, pyrolysis, natural zeolite, catalytic reformer, fuels

1. Introduction

In decades, plastic wastes have become a major stream in solid waste and caused significant environmental problems to human being. In most countries and regions, waste plastics are recycled and recovered by three ways: re-extrusion, mechanical, chemical and energy recovery⁽¹⁾. Pyrolysis, as one of the major categories of chemical recovery, which can minimize the environmental impact and alleviate energy shortage, has been introduced not only for waste reduction but also for energy recovery.

Pyrolysis or thermal cracking involves degradation of polymeric materials by heat in inert atmospheres. These pyrolytic products composed of liquid fraction, gas fraction and solid fraction. However, the degradation rate is relatively low. As such, the catalytic degradation of plastic waste has been investigated extensively by many researchers. The presence of catalyst indeed promotes the chemical reaction resulting in the selectivity toward specific products with high added value. However, high cost of catalyst is the other obstacle for pyrolysis of plastics. Natural zeolite, which can be found in many places worldwide, might be used as a promising alternative catalyst to lower cost associated with the usage of commercial catalysts. This study focused on the effect of HCl pretreatment on the catalyst performance of natural zeolite, and pointed out that the acid pretreatment of zeolite catalysts tends to affect the composition of pyrolytic products. The X-ray analysis technique, SEM and the BET analysis were employed to characterize the properties of the natural zeolite. The hydrocarbon analysis of oil products was completed by GC-MS.

2. Materials and Methods

2.1 Materials

The catalysts used for these experiments were the natural zeolite (NZ) obtained from Klaten, Indonesia and the HY-zeolite (CBV 780) came from Zeolyst International Company. Polypropylene (PP) and polystyrene (PS) granules were provided by Tosoh Co., Ltd in Japan. HCl and distilled water were obtained from Wako chemicals.

2.2 HCl pretreatment of catalyst

Four types of natural zeolite (NZ) and one commercial zeolite catalyst (HY-zeolite) were used in the pyrolysis of

polypropylene (PP). The raw natural zeolite was ground, sieved to 100 mesh particles size and washed with distilled water at room temperature to remove the water soluble impurities. The washed NZ was dried in muffle furnace at 120 °C for 5 h and calcined at 500 °C for 3 h, which was named as NZ and used as the first catalyst. The NZ sample was also the raw material in the subsequent treatment steps.

As for the HCl pretreatment, the acid treated form was prepared by mixing 20 g of NZ with 500 ml of 0.5M, 1 M or 6 M HCl solution under the reflux condition under the atmospheric pressure for 1 h. After the HCl pretreatment, the zeolite was filtered and washed with distilled water, after which it was dried at 120 °C for 5 h and calcined at 500 °C for 3 h. The products were named as 0.5M-NZ, 1M-NZ and 6M-NZ according to the concentration of HCl solution. The HY-zeolite was used as comparison.

2.3 Pyrolysis and catalytic reforming of plastics

In this step, pyrolysis and catalytic reforming process of PP and PS were carried out in a two stage system as shown in Fig.1, which consisted of pyrolyzer and catalytic reformer. The pyrolyzer with inner diameter and height of 30 mm and 250 mm was made of stainless steel. It was wrapped up in an electric heater. The stainless steel reformer with inner diameter and height of 10 mm and 250 mm was also wrapped up in an electric heater. At the outlet of the reformer, a water-cooled condenser was installed to cool and separate gas and liquid products.

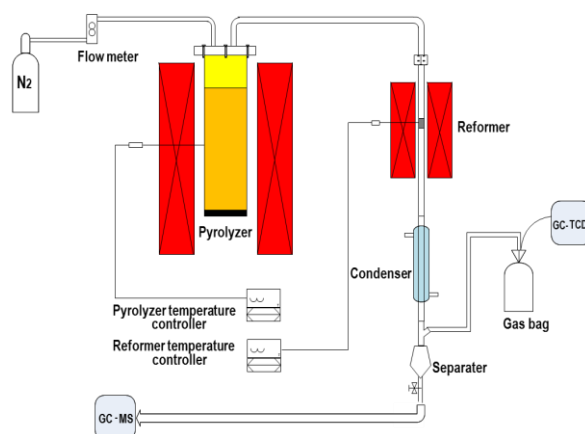


Fig.1. System flow of experiment facility

50 g of the feedstock and 1 g of the catalyst were placed in the pyrolysis reactor and the reforming reactor, respectively, beforehand. First, the reformer was heated up to 450 °C to removal the moisture in the catalyst and the air in the reactors was replaced with N₂ carrier gas (100 ml min⁻¹) at the same time. The feedstock was heated in the pyrolyzer at 500 °C, and then the vapors went through the catalytic reformer. After finishing the catalytic reaction, the gas was cooled to recover liquid products in the condenser. Liquid products were collected and weighed, and gaseous products were collected in a gas-sampling bag. All the experiments were implemented under the same operation conditions. To evaluate the performance of the catalysts, experiments with HY-zeolite and without any catalysts were also conducted with the same procedures.

2.4 Characterization of catalyst and product

The crystalline structure of the natural zeolite before and after the HCl pretreatment was determined by the X-ray diffractometer for pole point figure measurement (X'Pert-MPD-OEC). The surface microcosmic appearance and the three dimensional structure of catalysts was observed by the Field emission gun scanning electron microscope (FE-SEM S4700). The chemical composition and the Si/Al ratio of catalyst samples were confirmed by the X-ray Fluorescence (XRF) analyzer. The BET surface area was detected by the nitrogen adsorption-desorption measurements, which were measured at 77 K on a Belsorp-mini II. The liquid product composition was analyzed by GC-MS, and the gaseous product composition was measured by GC-TCD (Agilent Technologies Inc. USA).

3. Results and Discussion

3.1 Characterization of catalysts

The XRD analysis has been done, in order to examine the change of the pore structure in the NZ and its HCl pretreated, and HY-zeolite samples. The concentrated peaks shown in Fig. 2 indicated that this natural zeolite samples has regular crystal form. The main structure of the NZ catalyst could be identified to be mordenite type by three characteristic peaks 2 θ (degree) = 25-30. Most of the peaks observed at 2 θ (degree) = 5-35 also proved this estimate. According to the XRD results of the HCl pretreated sample, we can infer that the HCl pretreatment could remove a part of impurities, but would not destroy the main crystalline structure. The chemical composition and the BET surface area for natural zeolite before and after the HCl pretreatment are listed in Table 1. It can be seen that the HCl pretreatment of NZ could increase the Si/Al ratio. The surface area also increased with the increase of the concentration of HCl solution.

In the BET surface case, it changed a lot from NZ to 1M-NZ. However, the difference is not so obvious between 1M-NZ and

Table.1. SiO₂/Al₂O₃ mole ratio and BET surface area of HY-zeolite, NZ before and after the HCl pretreatment.

	SiO ₂ /Al ₂ O ₃	Pore Volume(cm ³ /g)	SBET
NZ	8.12	679.	91.1
0.5M-NZ	-	-	174.0
1M-NZ	13.02	83.26	233.9
6M-NZ	24.55	89.84	282.1
HY-zeolite	80.00	-	780.0

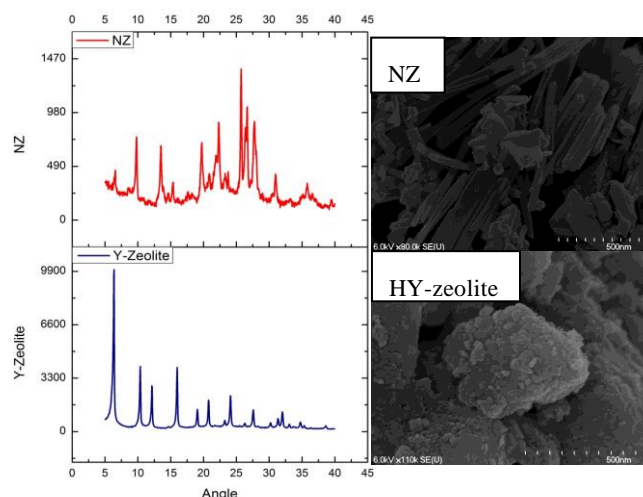


Fig.2. X-Ray powder diffraction pattern and the SEM images of natural zeolite and HY-zeolite samples.

6M-NZ. In consideration of the cost factor and unobvious effect of 6M HCl, pretreatment by 1 M or below HCl solution is more attractive.

3.2 The product yield of polypropylene

According to Fig.3., all of the liquid yields were over 85%. However, there is a trend that the liquid yield from polypropylene increased with the increase of the concentration of HCl pretreatment solution.

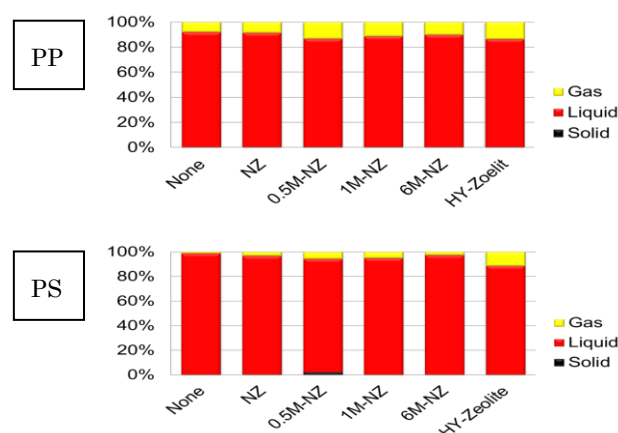


Fig.3. Product yield obtained from the pyrolysis and catalytic reforming of polypropylene and Polystyrene.

4. Conclusions

The natural zeolite used in this experiment belonged to mordenite type. The HCl pretreatment could increase the Si/Al ratio and the surface area of natural zeolite. Concentration range of HCl solution not higher than 1M was identified as an appropriate range. The liquid yield from polypropylene and polystyrene increased with the increase of the concentration of HCl pretreatment solution, but not very obvious. The composition of liquid products changed a lot with the the concentration of HCl solution.

5. References

[1] S.M. Al-Salem, P. Lettieri, and J. Baeyens. Resources, Waste Management 29 (2009) pp. 2625-2643.