Continuous catalytic cracking of plastics using fluidized bed
− Activity of the metal oxide catalyst –

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Abstract: The catalytic cracking reaction of polyethylene or polypropylene was carried out using Mn_3O_4 and Co_3O_4. As a result, hydrocarbons and CO were obtained: for example, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and C_4H_n. The gasification rate was higher for Co_3O_4. The total produced amount of the formed hydrocarbon gas was compared for each reaction temperature, it was 650 °C > 700 °C > 600 °C. The polyethylene and polypropylene decomposition activity showed the maximum at 650 °C. Polyethylene produced more hydrocarbon C_2 by catalytic cracking. Polypropylene produced more CH_4 and hydrocarbon C_3 by catalytic cracking.

Keywords: Waste plastic, Catalytic cracking reaction, Metal oxide catalyst.

1. Introduction

An about 12 million-ton waste plastic per year is discarded, parts are collected for reuse for the purpose, and recycling has been an important issue in Japan now. On the other hand, hydrocarbon and CO will be obtained if catalytic cracking of the waste plastic is carried out. [1][2][3] The method of using the gas obtained by gasification of the waste plastic as an auxiliary heat source of a manufacturing facility etc is innovative technology at the point that energy can be obtained, reduces CO_2 amount of emergence. [4][5]

In this study, catalytic decomposition of plastics was carried out using a fluidized bed reactor in order to improve gasification of waste plastics. The experiment was conducted by changing the reaction temperature and catalyst, we examined the activity of Mn_3O_4 and Co_3O_4.

2. Experimental

Catalyst: Mn_3O_4, Co_3O_4 were mixed and used for 1.0 g and fluid sand (10.0 g). Fluid sand used a CARiACT (FUJI SILYSIA CHEMICAL, Ltd., Q-3, size 75 - 150 μm).

Sample: Polyethylene was manufactured by ALDRICH (low density, Size 2.8 - 3.5 mm), denoted as PE. Polypropylene was manufactured by ALDRICH (Isotactic, Size 1.8 - 2.5 mm), denoted as PP.

Reaction: The fluid bed type reaction apparatus was used. Fluid sand and a catalyst were put in the quartz tube reactor (inner diameter, 18 mm), and gas was supplied from the bottom. The reactant gas (CO_2 30%, H_2 30%, and Ar 40%) flowed in 60 $ml \cdot min^{-1}$. The temperature of a reactor was raised to 600 °C, 650 °C or 700 °C, the catalyst was reduced and reacted 40 minutes later. PE and PP was dropped to the fluid bed from the rotary feeder in the reaction apparatus upper part. Outflow gas from reactor was analyzed by GC (TCD).

3. Results and discussion

The PE and PP catalytic cracking reaction advanced and hydrocarbons, such as CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_n, formed. In addition, the CO_2 included in the feed gas was reduced partly, and CO was formed. Besides, more than hydrocarbons C_6 of liquid were produced. After comparing the rate of gasification according to a catalyst, Co_3O_4 was the highest. When using any catalyst, olefin formed more than paraffin. It is thought that this is because the hydrogenation ability of the catalyst is low. Experimental results of reaction temperature change, the gasification rate was better 650 °C than 700 °C. At high reaction temperature, soot adhered to the inside of the quartz tube reactor. It is considered that the hydrocarbon was thermally decomposed and converted to carbon.

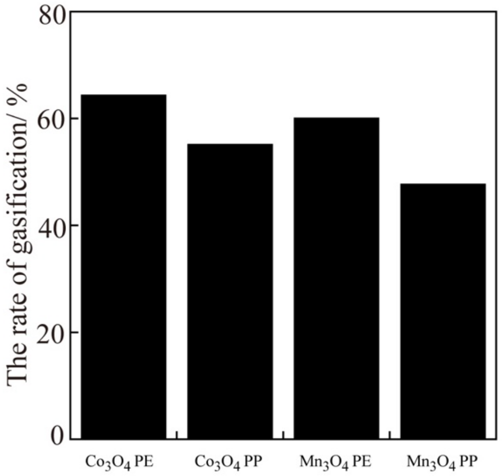

Figure 1. The rate of gasification of hydrocarbon in each catalyst at reaction temperature 650 ° C.

Then, the gasification ratios of PE and PP are compared. Change of the gasification made from PE or PP decomposition of each catalyst at 650 °C when CARiACT is used for fluid sand is shown in Fig. 1. The gasification rate was higher PE than PP in any of the catalysts. In PE, Hydrocarbons C_2 is generated more PE than PP. However, ratio of the hydrocarbons C_3 was less than the ratio of the hydrocarbons C_2. Since PE is the plastic in which C_2H_4 polymerized, it is thought that hydrocarbons of C_2 were easy to be formed in comparison with PP at the time of catalytic cracking.

In case of PP, C_3 hydrocarbons was generated more the PP than the PE. When using any catalyst, C_3 hydrocarbons was generated more PP than PE. However, ratio of the C_2 hydrocarbons was less than the ratio of the C_3 hydrocarbons. Since PP is the plastic in which C_3H_8 polymerized, it is thought that hydrocarbons of C_2 were hard to be formed in comparison with PE at the time of catalytic cracking. Moreover, when the outlet gas concentration of each gas was measured, the concentration of CH_4 was high from PE. The structure of PP has added the methyl group to the structure of PE, the result of this is considered that many CH_4 are generated compared with PE at the time of catalytic cracking.

As a result of conducting XRD analysis of the catalyst in front of a reaction, Co_3O_4 did completely have reduction to Co. On the other hand, Mn_3O_4 was reduced to MnO. It is considered that Co and MnO are related to the catalytic cracking reaction.

4. Conclusions

When the gasification rate by catalytic cracking with the catalyst of PE and PP was compared, the gasification rate was high in order of $Co_3O_4 > Mn_3O_4$. The total produced amount of the formed hydrocarbon gas was compared for each reaction temperature, it was 650 °C > 700 °C > 600 °C. When reacting at 700 °C, the amount of hydrocarbon gas decreased. As for the outlet gas concentration of hydrocarbon, in PE, about 2 times the amount C_2H_4 was generated to C_2H_6. PP produced more CH_4 and C_3 than PE. As a result of conducting XRD analysis of the catalyst in front of a reaction, Co_3O_4 did completely have reduction in Co. On the other hand, Mn_3O_4 was reduced to MnO. Co_3O_4 and Mn_3O_4 had changed to Co and MnO before reaction. From the analysis results, Co and MnO are related to active species of carbon bond cleavage.

References

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