

## Reaction Control in Radical-Transforming Catalytic Degradation of Polypropylene using Fe Supported Active Carbon Catalyst under High H<sub>2</sub> Pressure

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The functions of Fe and A.C. were examined in catalytic degradation of PP under H<sub>2</sub> atmosphere by comparing Fe/A.C. with Fe/SiO<sub>2</sub> and A.C. as a catalyst. Fe promotes the consumption of H<sub>2</sub> to decompose solid product. A.C., of which surface is rich in radicals, degrade heavy oil to produce light oil. As a result, liquid yield in case of Fe/A.C. was the maximum and the degradation of liquid product was most promoted.

### Introduction

The increasing amount of waste plastics has caused serious environmental problems. Therefore, the recycle technologies have lately attracted remarkable attention and have been studied from several points of view. Most especially, liquefaction technologies of plastics to convert into chemicals or fuels, which are called chemical recycle or feed stock recycle are assumed to be some of the most promising methods in the future for processing waste plastics.[1] And also these processes don't produce poisonous substance such as hydrogen chloride or dioxin into air because this recycle is conducted in closed system.

We have postulated a catalytic process of plastic degradation by using Fe on active carbon catalyst (Fe/A.C.) which had been developed for the cracking of residual oils to produce high quality distillates.[2,3] This catalyst is inexpensive and disposable, moreover, the coked catalyst can be burned off to get heat after the reaction. In the process, depolymerization of plastics is believed to be free radical chain reactions, and so using Fe/A.C. under high H<sub>2</sub> pressure is expected to control hydrocarbon radicals through its catalytic hydrogenation.[2] Of course, if plastic can be converted into high quality oil in one reactor, the process will be more simplified and its cost is expected being lower.

This time, we investigated the function of Fe and A.C. as a catalyst comparing Fe/A.C. with Fe/SiO<sub>2</sub> or A.C. and the effects of H<sub>2</sub> as a reaction gas on the product distribution and H<sub>2</sub>

consumption in the catalytic degradation of polypropylene.

### Materials and Methods

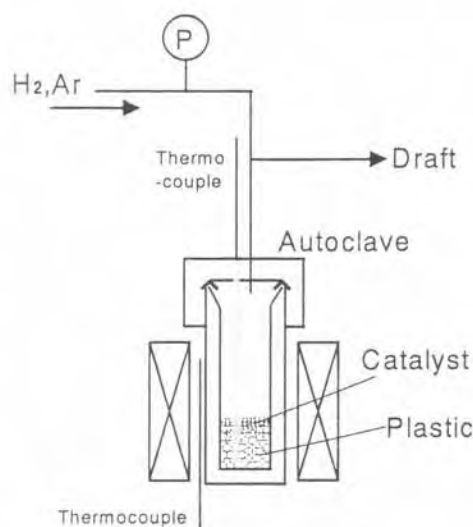
The PP used in this study was J 700 (Mitsui Chemicals Co., Ltd,  $M_n=54,000$ ,  $M_w=260,000$ ). It is beads-shaped and its diameter is about 3 mm $\phi$ .

Iron on active carbon catalyst(Fe/A.C.) was prepared by impregnating commercially available active carbon (20-40 mesh of Shirasagi G; Takeda Chemical Industries, Ltd) with ferric nitrate from its aqueous solution. Catalyst precursor was dried by heater with stirring and was dried in air at 393 K for 12 hours. This catalyst was reduced with pure H<sub>2</sub> (120 cm<sup>3</sup>/min) at 723 K for 1 hour and presulfided with 20 vol% H<sub>2</sub>S/H<sub>2</sub> gas mixture(120 cm<sup>3</sup>/min) at 673 K for 1 hour. The catalyst was crashed into particles with the size of <60 mesh before reaction.

Iron on silica catalyst (Fe/SiO<sub>2</sub>) was prepared by impregnating Aerosil SiO<sub>2</sub> with aqueous solution of ferric nitrate. Iron loading was 5 wt% as metal and its treatment was equal to Fe/A.C..

A.C. is just the same as mentioned before (Shirasagi G). This catalyst was used without any pretreatment and was crashed into particles with the size of <60 mesh before reaction.

Catalytic degradation of polypropylene(PP) was conducted in a batchwise autoclave with an inner volume of 70 cm<sup>3</sup> using a conventional shaking method (Fig. 1). At first, 15.0 g of PP and 0.0-0.9 g of the catalyst was charged into the reactor. After purging the inner air of the reactor with reaction gas (H<sub>2</sub> or Ar), the reactor was pressurized to 4.0 MPa with H<sub>2</sub> or Ar and heated up to reaction temperature with



**Fig. 1 Outline of Reactor**

Table 1 Boiling range of liquid products.

Naphtha(Nap.)	~ 443 K
Kerosene(Ker.)	~ 503 K
Gas Oil(G.O.)	~ 613 K
Vacuum Gas Oil(V.G.O.)	~ 798 K
Residue(Res.)	798 K ~

band heaters while being agitated at 70 times/min. At the end of the reaction period, the band heaters were removed and the reactor was cooled down to the ambient temperature in air. The reaction conditions were : reaction temperature; 673-693 K, reaction gas; H<sub>2</sub> or Ar, initial gas pressure; 4.0 MPa(NTP), reaction time; 0.5-5.0 hr.

The gaseous products were analyzed with a FID and TCD gas chromatograph (SHIMADZU GC 14B; Molecular Sieve 5A and Active Alumina). The liquid products were separated from solid products by suction filtration with aspirator. The boiling point distribution of the liquid product was obtained by simulated distillation (SIMDIS) using ASTM Method HT 750. Which was organized of HP 6890 gas chromatograph from Hewlett-Packard equipped with a crosslinked methyl siloxane capillary column (i.d.0.53 mm\*5 m). We determined the boiling point range as shown in Table 1. The residue from suction filtration was washed by toluene, dried in air and weighed as solid products.

## Results and Discussion

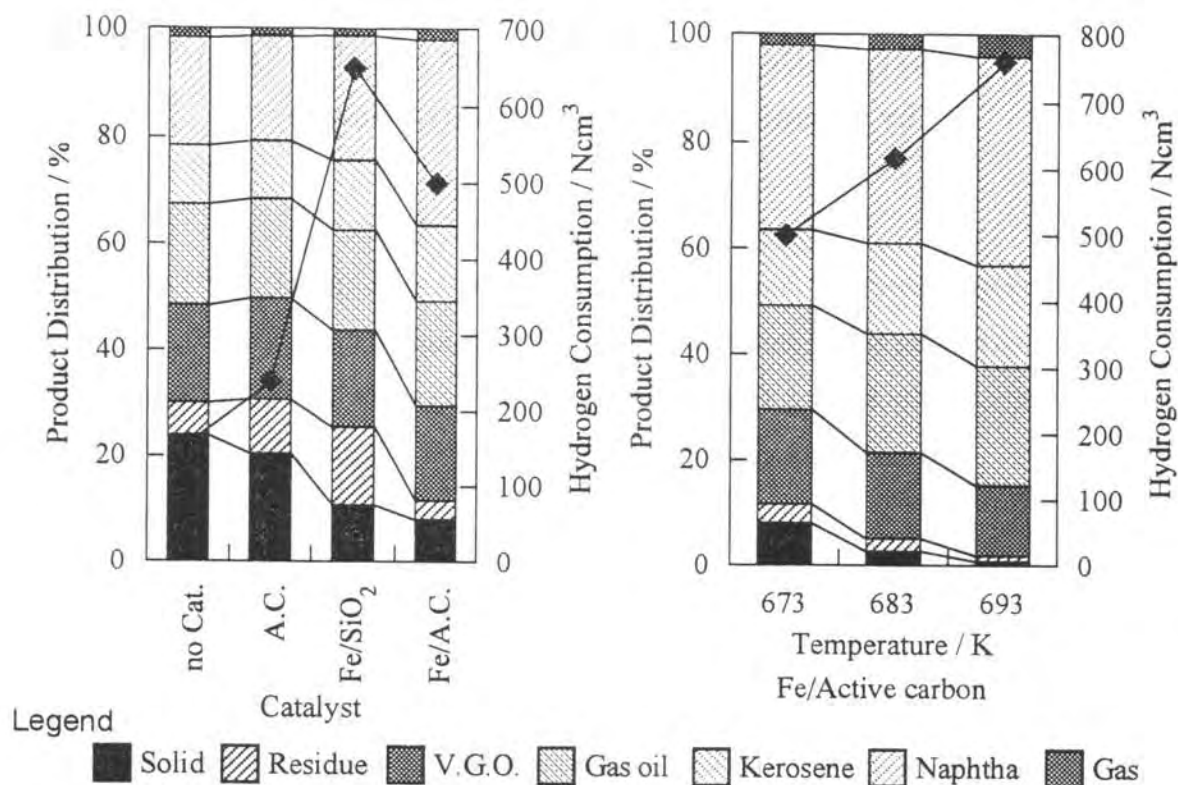
### 1. Effect of Catalyst

Fig. 2 showed the effects of the catalyst on the product distribution and H<sub>2</sub> consumption. The result with A.C. catalyst was very similar to that in thermal degradation and also H<sub>2</sub> consumption. It was thought that A.C. catalyst promoted the cracking of hydrocarbon to produce coke precursor or coke on the surface of A.C. and to seal the pores of charcoal surface. In the catalytic degradation with Fe/SiO<sub>2</sub>, the amount of solid product decrease a little, but that of residue increased as compared with the thermal degradation, and so, liquid product was very heavy oil. Hydrogenation of olefin is thought to be much promoted by Fe/SiO<sub>2</sub> catalyst as the result of large H<sub>2</sub> consumption.

Using Fe/A.C., gaseous product increased a little, solid product decreased, H<sub>2</sub> consumption was almost twice as large as that in thermal degradation and almost the same in catalytic degradation using Fe/SiO<sub>2</sub>. It was thought that the consumption of H<sub>2</sub> was promoted by Fe.

### 2. Effect of Reaction Temperature

Fig. 3 showed the effect of reaction temperature in catalytic degradation with Fe/A.C. catalyst. From these data, reaction temperature much affected to product distribution though it differed only 10-20 K. Compared the result in 683 K with in 673 K, solid product was decreased in about 20 point and the liquid yield was increased extremely. In 693 K, the decomposition of PP was promoted further to be light distillate. Naphtha yield was affected



**Figs 2-3 Effect of Catalyst and Temperature; Hydrogen 3.0 MPa(STP), PP 15.0 g, Catalyst 0.45 g.**

much by reaction temperature, but the yield of middle distillate such as gas oil, changed only little, because polymer was cracked step by step to heavy oil, to middle distillate, and finally, to light fraction.

### Conclusion

From these results, in case using Fe/A.C. in catalytic degradation of PP under high H<sub>2</sub> pressure, there exists most suitable conditions because of the balance between cracking of solid by Fe and of heavy oil by A.C..

### References

- [1] Chemical Engineering 1992, July, 30.
- [2] Nakamura, I.; Fujimoto, K. Catal. Today 1996, 27, 175-179
- [3] Nakamura, I.; Aimoto, K.; Nozaki, T.; Asano, T.; Fujimoto, K Prep. ACS 1993, 38(2), 324