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Development of new disposable catalyst for waste plastics treatment for high quality transportation fuel

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Abstract

An iron supported coal-derived active carbon catalyst showed excellent activity for liquefaction of polypropylene at low reaction temperature (380°C) to give colorless distillates selectively (98 wt.-%) in the presence of small amount of H_2S. Free radical on active carbon should initiate a cracking reaction by hydrogen abstraction to form a hydrocarbon radical. H_2S and $HS\cdot$ should promote radical transfer from the hydrocarbon radical to large size hydrocarbon molecule to suppress consecutive cracking of the hydrocarbon radical and to promote cracking of the large size molecule which cannot contact with solid catalyst.

Keywords: Waste plastics treatment; High quality transport fuel; Disposable catalyst

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1. Introduction

Liquefaction of waste plastics has been attracting great attention as a key technology to solve environmental protection problems. It has been reported that thermal cracking or acid catalyzed cracking could produce liquid product from plastics, such as polypropylene or polyethylene. However, results to date have produced oils which are waxy and of a very bad quality and, thus, are useful for very limited purposes.

The present authors have already reported a new coal-derived disposable catalyst developed for residual oils cracking to produce high quality distillates [1]. Both waste plastics and residual oil are made of high molecular weight hydrocarbons and usually contain impurities to poison catalysts. In this paper, cracking of polypropylene, which is a typical polyolefinic plastic, was conducted with the coal-derived catalyst.

2. Experimental

Catalysts were prepared by impregnating a variety of carrier materials with an aqueous solution of ferric nitrate. Iron loading was 5 wt.-% as metal. The catalyst precursor was dried in air at 120°C for 24 h. When CS_2 was not added to the autoclave before the cracking reaction, the catalyst was sulfided with a H_2–H_2S mixed gas (4/1 mol ratio) at 400°C for 1 h before the reaction. Carrier materials used were commercially available active carbon (Takeda HGS-616, made of wood, 1200 m^2/g), SiO_2–Al_2O_3 (Nikki chemical, Al_2O_3 28 wt.-%, 400 m^2/g) and a home made active carbon (660 m^2/g). The home made active carbon was prepared by treating Yallourn coal (brown coal) with carbon dioxide. Yallourn coal was heated in

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flowing carbon dioxide at a heating rate of 400°C/h to 600°C, held at 600°C for 1 h and activated at 850°C for 2 h.

Polypropylene (PP) cracking was conducted in a batch apparatus using a conventional shaking autoclave with an inner volume of 75 cm^3. The reaction conditions were: temperature; 380–400°C, reaction time; 1 h, initial hydrogen pressure; 3.0 MPa, PP; 10 g, catalyst, 0.3 g, CS_2; 0.03 g.

Gaseous products were analyzed by using a gas chromatograph. Boiling range of liquid products were determined by a distillation gas chromatograph for naphtha (IBP 171°C), kerosene (171-232°C), gas oil (232–343°C) and residue ($343°C^+$). Solid residue was determined to be n-pentane insoluble.

Dehydrogenation of methylcyclohexane (MCH) was conducted at 500°C using a pulse reaction apparatus in flowing nitrogen.

3. Results and discussion

The results of PP cracking with metal free active carbons and without a catalyst are given in Fig. 1. The Yallourn coal-based active carbon showed excellent activity for liquefaction of PP. The yield of distillate such as naphtha, kerosene and gas oil was in the order Yallourn > HGS-616 > Noncat. It should be noted that yield of gaseous hydrocarbon for Yallourn coal-based catalyst system was almost equal to those of a non-catalyzed system and commercially available active carbon system, whereas the liquefaction level was the highest in these systems.

Fig. 2 shows the ESR spectra of active carbons and MCH dehydrogenation activity. It is clear that the spin concentration of the home made active carbon derived from Yallourn coal is higher than that of a commercially available active carbon. Large number of free radicals were formed on the active carbon derived from Yallourn coal by the treatment with carbon dioxide. The free radical on the carbon surface should initiate the cracking reaction by abstraction of hydrogen especially tertiary hydrogen in PP shown as in Fig. 3. In other words, the cracking activity of an active carbon catalyst is determined by the ability to abstract hydrogen from hydrocarbon. In fact, the conversion level of MCH dehydrogenation for Yallourn coal based active carbon was higher than that of the commercially available one.

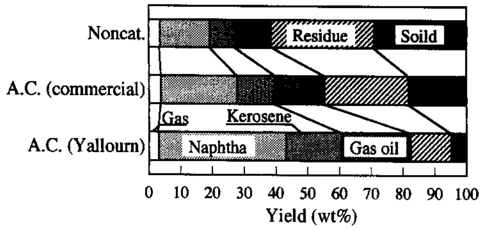

Fig. 1. Polypropylene cracking with metal free active carbon catalysts. Reaction conditions; initial hydrogen pressure; 3.0 MPa, 400°C, 1 h, PP; 10 g, catalyst; 0.3 g.

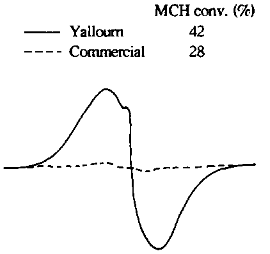

Fig. 2. ESR spectra of active carbons and MCH dehydrogenation activity.

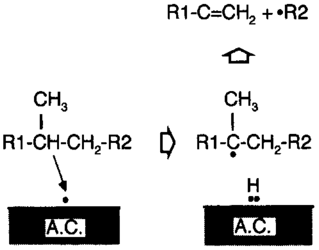

Fig. 3. Reaction model of hydrocarbon cracking on active carbon catalyst.

5 wt.-% of iron was loaded on active carbon to produce paraffin rich distillate, however, the Yallourn coal based active carbon showed excellent activity for PP cracking, and small amount of CS_2 was added for sulfurization of iron. In Fig. 4 are shown the product patterns of PP cracking with the iron supported Yallourn coal derived catalyst (Fe/A.C.) at 380°C.

In the absence of CS_2, Fe/A.C. system showed a little higher liquefaction level than that of the non-catalyzed system.

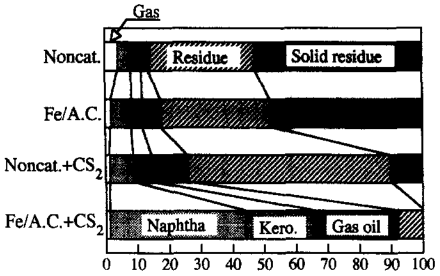

Fig. 4. Polypropylene cracking with a Yallourn coal-derived catalyst (Fe/A.C.) at low reaction temperature. Reaction conditions: initial hydrogen pressure; 3.0 MPa, 380°C, 1 h, PP; 10 g, catalyst; 0.3 g, CS^2; 0.3 wt.-%.

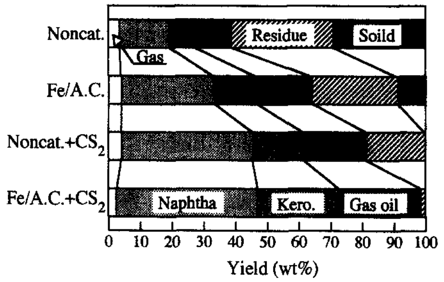

Fig. 5. Polypropylene cracking with a Yallourn coal-derived catalyst (Fe/A.C.) at high reaction temperature. Reaction conditions: initial hydrogen pressure; 3.0 MPa, 400°C, 1 h, PP; 10 g, catalyst; 0.3 g, CS_2; 0.3 wt.-%.

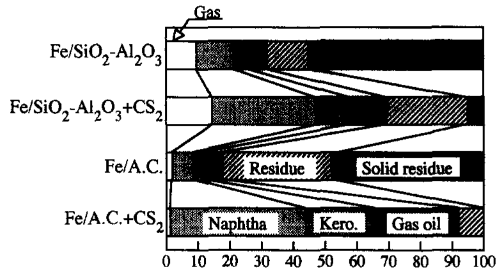

Fig. 6. Polypropylene cracking with a conventional hydrocracking catalyst. Reaction conditions: initial H_2 pressure; 3.0 MPa, 380°C, 1 h, PP; 10 g, catalyst; 0.3 g, CS_2; 0.3 wt.-%.

When small amount of CS_2 (0.3 wt.-%) was added, effects of the catalyst was shown clearly. In the Fe/A.C.–CS_2 system, little solid residue remained, yield of useful product such as naphtha, kerosene and gas oil was very high (92 wt.-%) and the liquid product was colorless. It has been reported that yield of gaseous products was 10–20 wt.-% to feed in thermal cracking or acid catalyzed cracking of PP. The yield of gaseous hydrocarbon was only 2 wt.-% on the Fe/A.C. in spite of the high cracking level. It was demonstrated that the iron supported active carbon catalyst had a potential to be an excellent disposable catalyst for waste plastics liquefaction, because it exhibited high cracking activity and very high selectivity for liquid products and the deactivated catalyst can be burned off to recover energy.

It should be noted that liquefaction level increased drastically not only in Fe/A.C. catalyzed system but also in non-catalyzed system by adding CS_2. It means that the role of the sulfur compound is not sulfiding iron on active carbon.

In Fig. 5 are shown the results of PP cracking at 400°C. Yield of liquid products increased with an increase in the reaction temperature, it reached 70 wt.-% even in a CS_2 free non-catalyzed cracking. In a CS_2 free system, effects of Fe/A.C. were shown more clearly than that at 380°C. It has been reported that the most favorable pore diameter for asphaltene cracking catalyst is 250 Å, because the average molecular weight of asphaltene is so high (5.0×10^3–10×10^3) [2]. On the other hand, most of the active carbon pores are micro or meso pores (under 100 Å), and the molecular weight of PP is 3.0×10^4–5.0×10^4. Therefore, it should be very difficult to liquify PP with Fe/A.C. alone shown in the results at 380°C. However, decomposition of PP proceeded thermally at 400°C and once the huge polymer molecule is cracked to moderate size molecules, they should be hydrocracked by solid catalysts, such as Fe/A.C., effectively to form naphtha, kerosene and gas oil.

Metal supported acid catalysts such as Ni–Mo/SiO_2–Al_2O_3 are used for hydrocracking of gas oil or vacuum gas oil. In Fig. 6 are shown the product patterns of PP cracking with Fe/SiO_2–Al_2O_3.

In the absence of CS_2, the amount of solid product in Fe/SiO_2–Al_2O_3 was more than that of Fe/A.C. and the yield of liquid product was 3/4 of the Fe/A.C. system. However, the yield of gaseous hydrocarbons of the Fe/SiO_2–Al_2O_3 system was 6 times that of the Fe/A.C. system. When small amount of CS_2 was added, liquefaction level of Fe/SiO_2–Al_2O_3 system increased drastically and became as high as that of Fe/A.C. Whereas the formation of gaseous hydrocarbon was not suppressed by adding CS_2 and the color of the

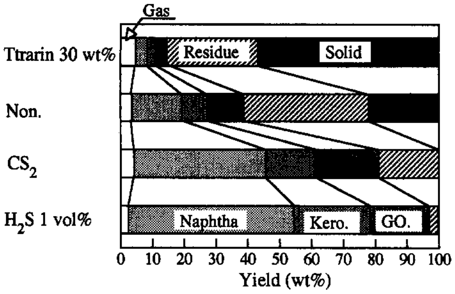

Fig. 7. Effects of sulfur compounds on the thermal cracking of PP. Reaction conditions: initial hydrogen pressure; 3.0 MPa, 400°C, 1 h, PP; 10 g, CS_2; 0.3 wt.-%.

liquid products was yellow, being different from that of the Fe/A.C.

These results suggest that the reaction mechanism of Fe/A.C. catalyzed PP cracking is different from that of a typical hydrocracking catalyzed by solid acid, namely it is a radical decomposition as mentioned before, and the life of the hydrocarbon radical is reduced by CS_2 to suppress the yield of gaseous hydrocarbon. The reason will be discussed later.

The results of both Fe/SiO_2–Al_2O_3 and Fe/A.C. showed a little activity for PP cracking in the absence of CS_2 at low reaction temperature suggesting that it is very difficult to liquefy PP, which is a very huge molecule, by solid catalyst alone.

In Fig. 7 are shown the effect of sulfur compound on non-catalyzed PP cracking. It is clear that H_2S was more effective than CS_2 for the liquefaction of PP. CS_2 should be converted into H_2S by the stainless steel wall of the autoclave in the presence of hydrogen and it should promote the selective liquefaction of PP. These results suggest that the role of sulfur compounds is not the sulfurization of iron catalyst, as mentioned before. However, FeS is a well known catalyst for coal liquefaction.

It is well known that hydrogen donor solvents, such as tetralin, are effective for liquefying coal, which is also a high molecular weight hydrocarbon [3]. The effect of tetralin on non-catalyzed PP cracking is also shown in Fig. 7. It was the exact reverse of that of H_2S, the cracking of PP was suppressed drastically by addition of tetralin. The role of tetralin in coal liquefaction have been understood as follows: Radical fragment formed during the liquefaction is stabilized by the hydrogen donation of tetralin to become a stable compound of lower molecular weight than the original coal. In the case of PP cracking, radical fragment formed during the liquefaction should be also stabilized by the hydrogen donation of tetralin. The stabilization is nothing but termination of the radical chain-reaction. The suppression of PP cracking should attribute to the simple stabilization of the radical fragment and the role of H_2S is different from that of the hydrogen donor solvent.

Effects of H_2S content on Fe/A.C. catalyzed PP liquefaction are shown in Fig. 8. The iron supported catalyst was sulfided with a H_2–H_2S mixed gas before the reaction. The distillate yield increased drastically by adding only a small amount of H_2S (0.08 vol.-%), but it was almost constant over 0.1 vol.-% of H_2S addition. It can be said that a very small amount of H_2S is enough to promote the liquefaction of PP.

In the series of the cracking reactions, amounts of H_2S in product gas were equal to those in the feed gas. Therefore, it can be said that the contamination of sulfur in product oil was only small. It has been reported that the iron supported active carbon showed comparable activity to molybdenum loaded active carbon catalyst in hydrodesulfurization of heavy oils [1]. In the PP cracking with H_2S, organo–sulfur compound may exist as an intermediate, which should be not thiophene but thiol or sulfide. However, such sulfur compound should be hydrodesulfurized by the iron supported active carbon catalyst easily in the presence of hydrogen to regenerate H_2S.

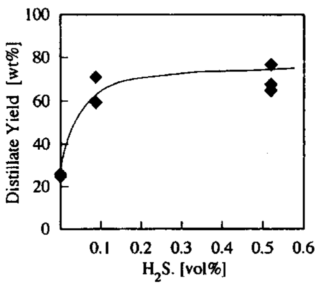

Fig. 8. Effects of H_2S content of Fe/A.C. catalyzed PP liquefaction. Reaction conditions: initial hydrogen pressure; 3.0 MPa, 390°C, 1 h, PP; 10 g, catalyst; Fe (5 wt.-%)/A.C..

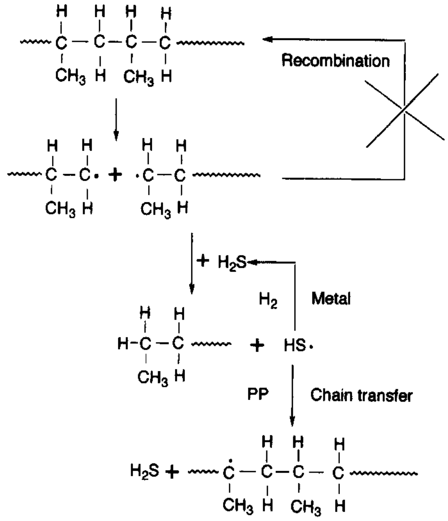

Fig. 9. Role of H_2S in PP cracking.

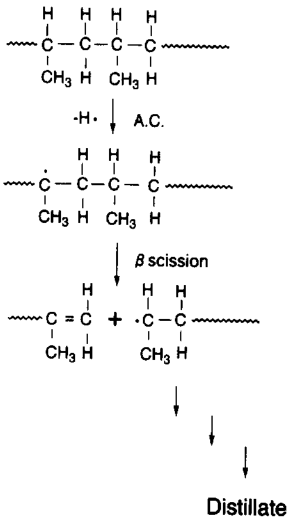

Fig. 10. Role of Fe/A.C. in PP cracking.

The roles of H_2S and Fe/A.C. in the hydrocracking of PP can be understood following the mechanism shown in Fig. 9 and Fig. 10. Hydrocarbon radicals are formed by thermal cracking of the C–C bond. The greater part of the radicals may recombine each other at low reaction temperature (380°C) in the absence of H_2S. In the presence of H_2S, H_2S may diffused into small openings of polymer structure and contact the hydrocarbon radical. Then hydrogen of the H_2S is abstracted by the hydrocarbon radical to form a stable hydrocarbon and HS·. The HS· should abstract hydrogen from the hydrocarbon such as PP or it is stabilized on the supported metal catalyst by hydrogenation. In the former case, radical concentration of the cracking system does not change whereas the life of the hydrocarbon radical is reduced. It means that the rate of the cracking reaction does not change and that the consecutive cracking of the hydrocarbon radical is suppressed to reduce the yield of gaseous products. Such chain transfer via H_2S or organo–sulfur compounds is a well known phenomenon in the radical polymerization of olefins [4]. Once a huge polymer molecule is cracked to moderate size molecules for solid catalyzed cracking, they can be hydrocracked by a solid catalyst such as Fe/SiO_2–Al_2O_3 and Fe/A.C. effectively to form naphtha, kerosene and gas oil. In the Fe/A.C. cracking, whose intermediate is not a carbenium ion but a hydrocarbon radical, as shown in Fig. 10, consecutive cracking of hydrocarbon radical is suppressed by radical transfer via H_2S to suppress the yield of gaseous hydrocarbon.

Acknowledgements

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