# Liquid Phase Cracking of Styrene Derivative Polymers with Metal Supported Carbon Catalysts.

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Cracking of styrene derivative polymers solved in decaline was conducted with metal supported carbon under an inert gas atmosphere for elucidating the detailed reaction mechanisms in liquid phase. As using metal supported carbon in this flow system, the monomer, dimer and trimer derived from the corresponding polymer were hydrogenated to saturated form in nitrogen atmosphere by hydrogen transfer reaction from decaline ,which was simultaneously dehydrogenated to tetraline and naphthalene with the evolution of hydrogen gas. In comparison with metal species, Pd and Ru supported carbon catalyst kept the hydrogenation activity for longer time and the lower evolution of hydrogen than Pt and Rh. The dehydrogenation of decaline was considered to occur mainly not on the metal surfaces but on the carbon surfaces over Pd supported carbon.

## Introduction

The disposal of mixed plastics waste poses a serious problem, because plastics are usually not bio-degradable. Landfill and incineration of plastic waste are a reasonably cheap way, but there are a few major problems to environmental considerations. So alternative methods for plastic waste recycling are currently being developed. Liquefaction method is one of the most promising alternatives[1]. In this method, polyolefins such as polyethylene(PE), polypropylene(PP) and polystyrene(PS) thermally degrade into low-quality fuels, which contain a lot of olefins. The reaction mechanism of pyrolysis was well discussed, although most research treated very small amount of polymer [2],[3],[4]. Then the products are improved by the catalytic process in order to upgrade the quality. Most researches have revealed an advantages of the catalytic process in which mostly solid acids are used[5],[6]. The olefins, however, deactivates the solid-acid catalyst markedly[7]. The olefinic hydrocarbons repolymerized to firm resin which gives out solid products as cokes on the catalyst. As the reaction progressed, carbonaceous products were accumulated on the tube reactor wall since the repolymerization of the formed monomer took place. Even if the thermal degradation products were used as a low-quality liquid fuel, the olefins would be unfavorable since they repolymerize. Uemich et.al reported on the formation of aromatics from PE and PP over the metal supported carbon catalyst [8]. They described that PE and PP was converted the aromatics *via* low molecular saturated or unsaturated hydrocarbons ,which formed by thermal degradation, with the evolution of the hydrogen gas. It indicates that the low molecular hydrocarbons derived from PE or PP are hopeful as hydrogen sources for the hydrogenation of styrene monomer derived from PS.

In present research ,we examine the hydrogenation of styrene derivatives derived from the corresponding polymers on metal supported carbon catalysts when decaline was used as a hydrogen source. We aim to use the plastic waste as a chemical resources and to convert the polyolefin mixture containing PE,PP and PS into alkylbenzene.

## Materials and Method

Polymers and solvents was used as received without purification.

A small amount of catalyst (ca. 0.5g) was placed into the tubular reactor for catalytic reaction. And the catalyst was activated at 723K for 2h in $H_2$ flow and then at 723K overnight in Ar before reaction. The liquid reaction mixture, composed of styrene derivative polymer (7-8 wt% , 0.5-0.7 mmol monomer unit/g) and decaline (6.7 mmol/g), was fed to the reactor under $N_2$ or Ar pressurized at 5 to 50 MPa. Contact time was 1-2 g of catalyst·h/g of polymer. Each run lasted 6h or more with sampling of the reactor effluent gas and liquid every 20 and 40 min respectively. For the effluent gas GC analysis was carried out using Ar as carrier gas, packed column system ,FID and TCD detectors. This systematic GC makes determination of $H_2$, $C_1$-$C_5$ hydrocarbons at a time possible. And for the effluent liquids from high pressure trapping vessel GC analysis was carried out using He as carrier gas, a HP-5 capillary column(5% phenylmethylsiloxane, 30m × 320 $\mu$ m × 0.25 $\mu$ m) and FID detector. Oven temperature programming was 323K for 5min, heating rate 10K/min up to 553K, maintained for 10min. Products identification was confirmed by GC/MS. In order to check the decreasing of the catalyst surface area after the reaction, the adsorption of *iso*-octane was measured by thermogravimetric analyser.

## Results and Discussions

### Hydrogenation of the monomer derived from the polymer

As using each metal supported carbon catalyst, the saturated form of the monomer was produced. These results suggested that decaline solvent was dehydrogenated and then the formed hydrogen atoms on catalyst surface transferred to the monomer, because most of the polymer is cracked thermally in the liquid phase to produce the monomer, dimer and trimer in this reaction system. Figure 1 illustrates the time course of the 4-*t*-butylethylbenzene, which was produced by hydrogenation of 4-*t*-butylstyrene formed from thermal cracking of the corresponding polymer, over each noble metal supported carbon catalyst. In this figure the time course of the 4-*t*-butylstyrene monomer shows too. We see from these figures that Pd and Ru supported carbon catalysts keep the better yield of 4-*t*-butylethylbenzene at a bout 70% for 10h ,on the other hand Pt and Rh catalysts indicate the reduction of the yield with the elapse of time. The evolution of hydrogen gas during the reaction over each catalyst is shown in figure2. The evolution is in fair agreement with a value calculated from a yield of naphthalene over each catalyst. Pt or Rh catalyst initially accelerated the dehydrogenation reaction, the activity of the dehydrogenation ,however, dropped down similarly to the yield of the 4-*t*-butylethylbenzene with the passage of time. Pd or Ru catalyst, by contrast, indicated the lower hydrogen evolution in spite of a high yield of 4-*t*-butylethylbenzene. And an increase of catalyst weight after the reaction for a constant time was less over Pd or Ru catalyst than over Pt or Rh. Furthermore the *iso*-octane uptake after the reaction decreased more over Pt and Rh than Pd and Ru.

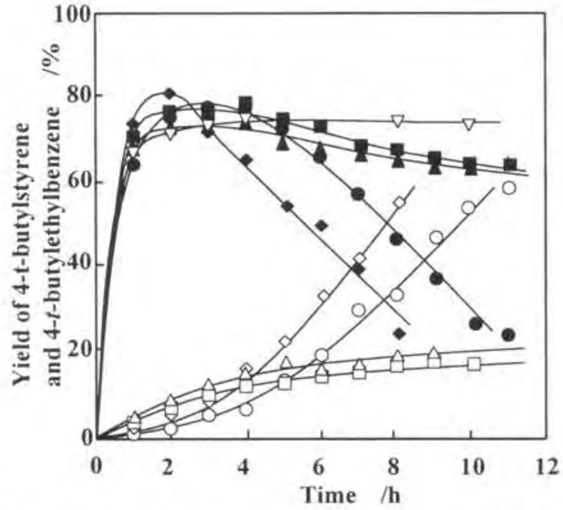

Figure 1 Time course of the monomer and its saturated form produced from poly-4-*t*-butylstyrene with metal supported carbon catalysts. W/F 1.4 g-cat·h/g-polymer,catalyst 0.5g, polymer/decaline 1/9 g/g, Ar 0.5MPa 6Nl/h, Temperature 450℃
4-*t*-butylstyrene ;▽non-cat,△Pd,□Ru,◇Pt,○Rh
4-*t*-butylethylbenzene ;▲Pd,■Ru,◆Pt,●Rh

Figure 3 shows the effect of supports for Pd catalyst. The activity for hydrogenating the monomer which formed *via* pyrolysis of the corresponding polymer was the highest over carbon support in comparison with $SiO_2$, $Al_2O_3$ ,zeolite Y and ZSM-5. Decaline was little dehydrogenated over each Pd supported catalyst except for Pd/carbon catalyst. Furthermore we found that the dehydrogenation of decaline could be proceeded on metal-free carbon catalyst. In addition, there have been some reports postulating radical intermediates for the cracking, dehydrogenation of alkanes over activated carbon[9],[10].

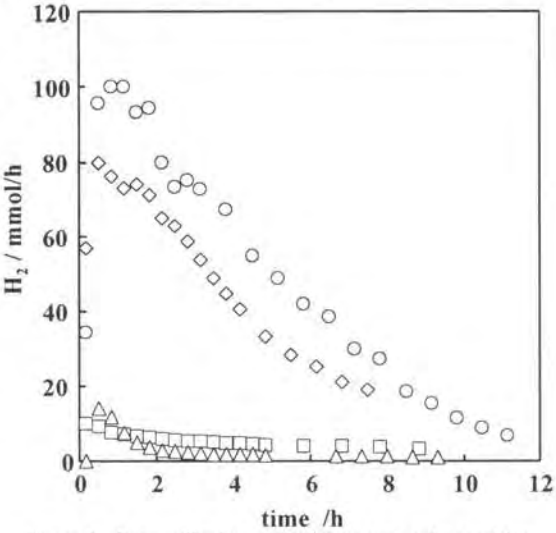

Figure 2 Rates of hydrogen evolution during the cracking reaction of poly-4-*t*-butylstyrene in decaline with metal supported carbon catalysts. W/F 1.4 g-cat·h/g-polymer,catalyst 0.5g, polymer/decaline 1/9 g/g, Ar 0.5MPa 6Nl/h, Temperature 450℃ △Pd,□Ru,◇Pt,○Rh

These results indicate that the dehydrogenation of decaline occurs not on Pd but on carbon support. Although the dehydrogenation of decaline is catalyzed on both metal and carbon support over metal supported carbon catalyst, the dehydrogenation would occur mainly on carbon support over Pd/carbon catalyst. Thus ,in analogy with Pd/carbon, the dehydrogenation of decaline would occur on carbon support over Ru/carbon. On the other hand , in the case of Pt or Rh supported carbon catalyst, it seemed that the dehydrogenation occurred on not only carbon but also metal. The reason why the activity of Pt or Rh catalyst dropped down is that coke deposition has occurred vigorously on Pt and Rh which have a high dehydrogenation activity .

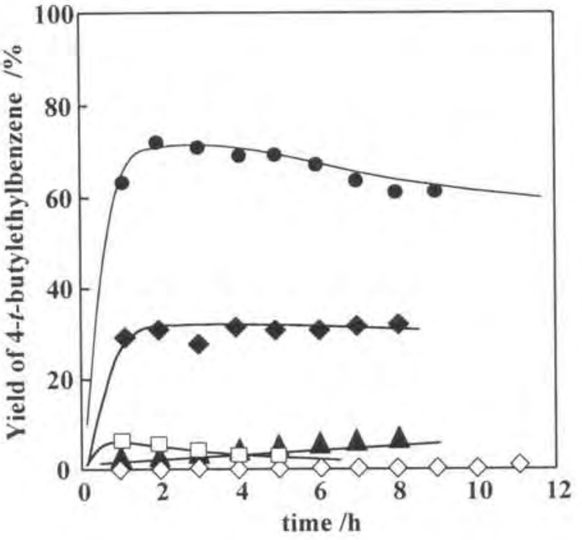

Figure 3 Effects of supports on time course of the 4-*t*-butylethylbenzene produced from poly-4-*t*-butylstyrene with Pd catalysts.
W/F 1.4 g-cat·h/g-polymer,catalyst 0.5g, polymer/decaline 1/9 g/g, Ar 0.5MPa 6Nl/h, Temperature 450℃
● Carbon, ◆ $Al_2O_3$, ▲ $SiO_2$, ◇ Y, □ ZSM5

Effect by the substituent

The polymers substituted at a 4 position such as poly-4-*t*-butylstyrene thermally degraded into the monomer ,dimer and trimer at the same composition as PS and the primary products were hydrogenated, although dealkylation has occurred on a few catalysts, the support of which has a acidity.

## Conclusion

In the system, most of the styrene derivative polymer is cracked thermally to produce the corresponding monomers, dimers and trimers. On the other hand ,decaline is dehydrogenated on metal supported carbon catalyst. The dehydrogenation occurs predominantly on the carbon support in the case of relatively low dehydrogenation-activity metal such as Pd. The hydrogen atoms formed on carbon support migrate on it to reach metal site and are consumed for the hydrogenation of the monomers.

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