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## 論 文 内 容 要 旨

### Chapter 1 INTRODUCTION

This chapter covers the background of the upgrading of heavy oil in cracking process, the coke deposition on a various catalysts and the characterization of the deposited coke. Then, the scope of this thesis is described.

The demand for middle distillate is increasing steadily and the demand for BTX is expected to grow through the coming years. Therefore, the upgrading of heavy oils becomes more and more important in supplying fuel and petrochemical feeds. However, the upgrading processes are suffering from the coke formation. Therefore, it is necessary to understand the mode of coke formation over catalyst. The work that will be presented in this thesis is dealing with such objectives.

The present work consists mainly of two parts; the first is about the upgrading of Orinoco tar to valuable chemicals such as BTX and the second part describes the characterization of the coke deposit produced in cracking of Orinoco tar and model compounds.

### Chapter 2 CATALYTIC HYDROCRACKING OF ORINOCO TAR OVER USY-ZEOLITE

In this chapter, the catalytic hydrocracking of Orinoco tar over USY-zeolite was studied using a high pressure fixed bed reactor to produce chemical feedstocks like BTX and oils. The effects of reaction temperature and the catalyst on the product distribution were examined. The main results and the conclusions obtained are summarized as follows.

This catalyst was found to be effective in increasing the yield of BTX from Orinoco tar. The yield of BTX about 19.4 wt % was achieved at 500 °C, as shown in Fig. 1. On the contrary, the yield of

light oil was lower in the catalytic hydrocracking than without catalyst. However, the quality was much better for the oil obtained in the catalytic reaction. It was found that the zeolite catalyst can keep its activity even though a considerable amount of coke was formed over the catalyst.

Although the extent of coking at 400 and 500 °C was similar, the nature of coke was different and thus the deactivation profile was also different. This result implies that the coke formation and the deactivation of catalyst are not necessarily related. It becomes clear that the understanding of the relationship between the coke formation behavior and the catalyst deactivation is essential for a better design of the reaction system. Then, the cracking reactions of n-hexane, benzene and naphthalene were carried out in the subsequent chapters.

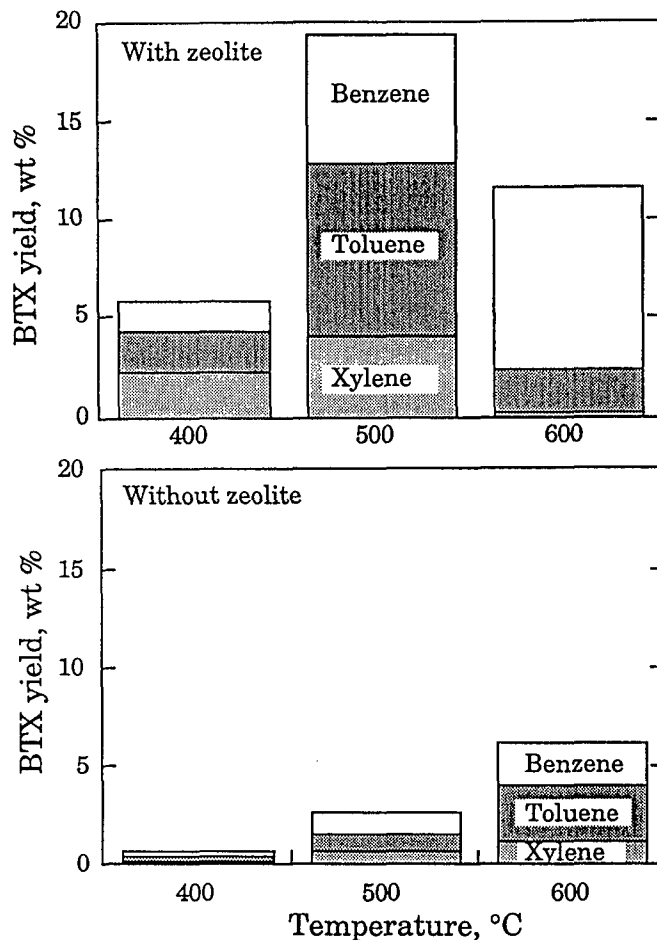


Fig. 1. Effect of temperature on the yield of BTX.

### Chapter 3 CATALYTIC CRACKING OF BENZENE OVER USY-ZEOLITE AND CHARACTERIZATION OF COKE

In this chapter, coke formation from catalytic cracking of benzene over USY zeolite was studied using a fixed-bed reactor at a different cracking temperature ranging from 500 to 800 °C under He or H<sub>2</sub>. The coke was extracted from the zeolite matrix by HF/HCl treatment. The effects of temperature, carrier gas, pressure on the structure of the coked zeolite and the extracted (liberated) coke were investigated. Nitrogen adsorption at -196 °C, SEM observation and elemental analysis were employed to characterize the coked zeolites as well as the liberated cokes. The principal results obtained in chapter 3 are as follows.

In He, a large amount of coke was deposited and the surface area of the catalyst decreased to a large extent. It was speculated that the coke was deposited mainly on the internal surface of zeolite catalyst. In H<sub>2</sub>, the extensive coking was observed at 800 °C, but the decrease of the surface area of catalyst was not so much. The surface area and the morphology of the coke produced in H<sub>2</sub> atmosphere was quite different from those obtained in He. It was concluded that the coke was deposited

mainly on the external surface of zeolite at high temperature. The effect of metal components found in Orinoco tar was examined on the cracking of benzene. It was found that the metals have little effect on the coking behavior under the present conditions.

#### **Chapter 4 CATALYTIC CRACKING OF n-HEXANE AND NAPHTHALENE OVER USY-ZEOLITE AND CHARACTERIZATION OF COKE**

In this chapter, the effect of the feedstocks on coke formation over the zeolite catalyst was studied. In addition to Orinoco tar and benzene, the cracking reactions of n-hexane and naphthalene were investigated. Naphthalene was used to check the effect of molecular size and n-hexane was used to check the difference in coke formation between the paraffin chain and aromatic ring. The coked zeolite and the liberated coke were characterized in the same manner as in Chapter 3 and these results from different hydrocarbons were compared each other. The following conclusions were obtained.

The coking characteristics in He of three hydrocarbons were not so different. The morphology of liberated coke was quite similar to those of corresponding coked zeolite and fresh zeolite, and thus it was concluded that the coke was deposited mainly in the zeolite channels. In H<sub>2</sub>, the result for naphthalene cracking was somewhat different from others, but as a whole the effect of the type of feedstocks was rather small. Therefore, the information obtained in such model reactions can be applied to designing the reaction of Orinoco tar.

#### **Chapter 5 CONCLUSIONS**

This chapter describes the general conclusions of this thesis. From the results in Chapter 2, USY-zeolite was found to be effective in increasing the yield of BTX from hydrocracking of Orinoco tar. A high yield of BTX of 19.4 wt% was achieved at 500°C. The relationship between the deactivation and the amount of the coke was not straightforward. From the results observed in the model reactions (Chapters 3 and 4), it was concluded that the coke formation behavior was essentially the same for different feedstocks, but it was quite different between catalytic cracking in He and in H<sub>2</sub>. In inert atmosphere, most of the coke was deposited in the catalyst pore, while in H<sub>2</sub>, the coke formation was less abundant. Therefore, it would be possible to use zeolite catalyst as a hydrocracking catalyst if one can find the optimum reaction condition where the amount of the coke is small and its location is limited only on the external surface. Under such conditions, the USY-zeolite would keep its activity even some coke were deposited on its surface.

## 審査結果の要旨

今後の石油供給の緊迫化に対処するため、未利用重質炭化水素の有効利用に期待がかかっている。著者は、ヴェネズエラに大量に賦存しているオリノコタールの利用に注目し、付加価値の高い化学原料、あるいは軽質燃料油への転換技術を確立するための研究を行った。具体的には、触媒を用いた水素化分解による軽質化を試み、ベンゼン、トルエン、キシレン成分、および良質な軽質油を高収率で得ることに成功している。さらに、これまで研究例のない 500℃以上という高温でのコークの生成機構についての検討も行った。本論文は、これらの研究成果をまとめたもので、全文5章よりなる。

第1章は序論であり、本研究の背景および目的を述べている。

第2章では、USY ゼオライトを用いたオリノコタールの水素化分解反応について記述している。500℃、5 MPa の加圧水素下で反応を行い、触媒を用いることによりベンゼン、トルエン、キシレン成分を 20wt% の高収率で得ることに成功し、触媒を使用することにより良質の軽質油成分が得られることを見出している。コーク生成による触媒失活は、このような反応系の最大の問題点であるが、今回の条件下では 400℃ 程度の温度領域ではげしい失活が認められたものの、500℃以上では失活の程度は軽微であった。

第3章では、モデル物質としてベンゼンを用い、ゼオライト上へのコーク生成反応、ならびに生成したコークの性状を解明する試みを行っている。これまでこのような高温領域でのコーク生成の研究がほとんど見られないためである。反応後のコーク付着ゼオライト、および酸処理によりゼオライトを溶解除去したコークの双方について、表面積・細孔容積測定、電子顕微鏡観察などを行うことにより、コーキング機構の解明を行ったところ、不活性ガス雰囲気下では、コークが主としてゼオライトの細孔内に堆積するのに対し、水素雰囲気下では細孔内にはあまり堆積していないことを見出した。このことが、触媒失活が非常に少ない原因であり、今後の反応設計を行うにあたり、重要な知見を与えるものである。

第4章ではさらに、脂肪族炭化水素、および環数の多い芳香族炭化水素としてヘキサン、ナフタレンを選び、コーキング反応を行っている。これらに、オリノコタール、ベンゼンの結果も合わせてコーキングに対する原料の違いを検討している。その結果、反応条件により若干の差があるものの、コーキングの程度、生成したコークの性状は原料によって大差ないことを見出している。

第5章は結論である。

以上要するに本論文は、オリノコタールの水素化分解における USY ゼオライトの有効性を見出し、高収率でベンゼンなどの化学原料を得ることができることを示すとともに、これまで研究のなかった高温領域におけるコーク生成機構を詳細に検討したもので、有機資源化学の発展に寄与することが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。