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Hydrocracking of Polycyclic Aromatic Hydrocarbons Catalyzed by Three Nickel-supported Different Zeolite Catalysts

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Hydrocracking of phenanthrene and pyrene over three different types of Ni-loaded zeolite catalysts (ZSM-5, Mordenite, and Y-type) was performed. The reaction conditions were as follows: 350°C, 70 kg/cm² (H₂), 0, 15, 60 min. The presulfided Ni-Mo catalyst was also examined for comparison. Among the three zeolite catalysts, clear-cut differences in product distribution were observed. In the case of phenanthrene, the extent of cracking depended upon the pore size of the catalysts. When ZSM-5 catalyst was used, a predominant production of dihydro-, tetrahydro- and *sym*- and *unsym*-octahydrophenanthrenes took place because phenanthrene could not enter the channel pores of these catalysts. In the case of Y-type zeolite and mordenite, hydrocracking of phenanthrene skeleton proceeded more efficiently. The presulfided Ni-Mo catalyst was observed to be excellent for hydrogenating these polyaromatic compounds, but no cracking reaction was observed. In the case of using pyrene as a substrate whose molecular size is larger than the pore size of the channels of the zeolites employed, similar effects of pore size on product distribution were observed. Combination of the presulfided Ni-Mo catalyst and Y-type zeolite was examined to obtain high yields of mono- and diaromatic compounds from pyrene, and the results observed were briefly discussed.

1. Introduction

The coal tar obtained from coal carbonization is a treasure trove of polyaromatic hydrocarbons, in which more than 400 kinds of aromatic compounds are found¹⁾. Naphthalene, whose yield is about 9.0%, is used for production of phthalic anhydride, dyestuff, pharmaceutical products and synthetic resins. On the other hand, the utilization of phenanthrene and pyrene, whose yields are 5.0% and 2.1%, respectively, has so far been limited to production of carbon black and antiseptics of timbers.

The application of these aromatic compounds for starting materials of fine chemicals is not yet developed extensively. To develop new catalysts capable of converting ultimate three or four ring aromatics into mono- or di-aromatic compounds is one of the objectives of polyaromatics utilization. Hydrocracking of polyaromatic compounds appears to proceed *via* the formation of terminal-naphthenic ring of the starting aromatic compounds, followed by the cleavage of the naph-

thenic ring to produce alkylated aromatic compounds, which have less number of rings than the starting aromatics. Accordingly, hydrogenation of aromatic rings and cracking of the resulting naphthenic rings are the key steps in hydrocracking, thus such dual-functional catalysts as metal-supported acid ones are considered to be some of the best candidates^{2)~12)}.

In a previous paper¹³⁾, we conducted hydrocracking of phenanthrene over H-Y, La-Y, Fe-Y, and Ni-Y zeolite catalysts and found that Ni-Y zeolite catalyst showed the highest activity among the catalysts employed (400°C, 1 h, and 70 kg/cm² of H₂). In the related paper¹⁴⁾, we introduced the results of our CAMD study on product distribution of the liquid products from hydrocracking of phenanthrene and pyrene on Ni-loaded ZSM-5, mordenite, and Y-type zeolite catalysts. The present paper deals with the effects of the variables on the extent of hydrocracking of phenanthrene and pyrene using the above three catalysts, followed by detailed analysis of the products consisting of gaseous and liquid products and coke. The mechanism of this hydrocracking reaction is also considered.

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2. Experimental

2.1. Preparation of Nickel-supported Zeolites

Each of the three kinds of NH_4 -substituted zeolites (50 g) was stirred in 1000 ml of aqueous solution of $\text{Ni}(\text{NO}_3)_2$ (0.25 M), at 90°C for 96 h, then filtered and dried at 110°C to obtain a nickel cation substituted zeolite. The catalyst was calcined in a stream of air at 500°C for 4 h, then reduced with H_2 atmosphere at 450°C for 1 h. The content of nickel in the zeolite was determined using a Rigaku Denki System 3270 type fluorescence X-ray analyzer. The distribution of acid sites in the catalyst was measured by using the temperature programmed NH_3 desorption technique: catalyst was first, dried at 600°C , then treated in a stream of NH_3 at 110°C to absorb NH_3 on the catalysts. The catalyst thus treated was cooled to 50°C , then heated to 610°C with the rate of $4^\circ\text{C}/\text{min}$ in He atmosphere. The amount of NH_3 desorbed was quantitatively analyzed by gas chromatography.

2.2. Hydrocracking of Polyaromatic Hydrocarbons

Polyaromatic hydrocarbon (1 g) and the nickel-supported zeolite catalyst (0.5 g) were placed in a 70 ml SUS 316 autoclave, which was pressurized to $70\text{ kg}/\text{cm}^2$ with hydrogen and heated up to about 350°C at a rate of $8^\circ\text{C}/\text{min}$. Reaction time here means the duration of reaction at 350°C . Therefore, 0 min of reaction time is with the run where the autoclave was taken out of the furnace and quenched to room temperature with an air blast. After the gaseous product was collected, its aliquot was submitted to GC analysis with a Shimadzu GC-3BT (active carbon column, 2 m) and a Shimadzu GC-8AIT (silica gel column, 60/80 mesh, 3 m). The liquid product was recovered by washing inside of the autoclave with CH_2Cl_2 . According to the analysis by a JEOL JMS-DX-303HF type GC-MS and/or according to the reported results of analysis of anthracene oil¹⁵⁾, and the components of the liquid product were assigned by quantitative analysis conducted with a Shimadzu GC-14APFSC (CBP-1 capillary column, 0.5 mm (dia.) $\times$ 25 m). The carbon deposited on the catalyst was evaluated based on the microanalysis of the recovered catalyst.

3. Results and Discussion

3.1. Characterization of Nickel-supported Zeolites

The contents of nickel in Y-type zeolite ($8\text{\AA}$), mordenite ($7\text{\AA}$), and ZSM-5 type zeolite ($5.5\text{\AA}$), based on the measurements by X-ray fluores-

Fig. 1 NH_3 -TPD Profile for Three Zeolite Catalysts

cence, were found to be 3.11, 1.77, and 1.22 wt% respectively. The number in parentheses indicates the pore diameter of zeolite channel. The results suggest that the larger the size of the pore is, the higher is the concentration of nickel on the catalyst when similar preparative methods for the zeolites were used.

The temperature profile of NH_3 -TPD is shown in Fig. 1. It is well known that TPD profiles of protonated zeolites show two maximum curves at around 200°C and in the range of 400 – 500°C ¹⁶⁾, respectively, indicating that zeolite has two different types of acid sites¹⁶⁾. From such observations, the amount of acid sites in these zeolites follows the order: ZSM-5 < mordenite < Y-type.

9,10-dihydro- (○), 1,2,3,4-tetrahydro- (●), *sym*-octahydrophenanthrenes (□), alkylated benzindans (■), alkylated tetrahydrobenzindans (Δ), *sym*-octahydroanthracene (▲), and alkylated phenanthrenes (+).

Fig. 2 Time Profile of Yield of Hydrogenated and Isomerized Phenanthrenes

Table 1 Results of Hydrocracking for Phenanthrene

Catalyst		Ni-Y (3.11)	Ni-Y (3.11)	Ni-Y (3.11)	Ni-Y (1.33)
Reaction time	[min]	0	15	60	60
Product distribution	[wt%]				
Gas		5.1	15.2	67.5	44.5
	ethane	1.8	1.3	3.2	0.7
	propane	1.0	6.9	24.2	15.5
	<i>i</i> -butane	2.0	3.6	17.0	10.7
	<i>n</i> -butane	0.3	3.4	23.1	17.6
Liquid		15.6	49.2	31.3	43.7
Deposited carbon		8.2	10.4	10.1	11.1
Recovery of phenanthrene		79.6	15.9	0.7	3.1
Total ^{a)}		108.5	90.7	109.6	102.4
Hydrogen consumption		8.7	11.2	16.1	14.4
Distribution of liquid products	[wt%]
16.3	5.3	1.9	3.3
15.1	7.9	0.9	1.7
0.4	3.9	1.1	1.5
7.0	1.3	3.1
0.4	12.5	4.5	7.3
5.2
50.9	10.5	0.8
1.0	16.5	34.8	41.9
1.4	0.3	0.5
5.9	15.0	11.7
3.3	27.2	20.1

a) Total means the sum of wt% of each fraction (liquids, deposited carbons, phenanthrene recovered, and gaseous products). Each fraction has specific error involved in its measurement so normalization to 100% was not used.

Strengths of the acid sites also follow the above order. Ni-Loaded catalysts also showed such TPD profile as cited above, and the amount of acid sites was found to show an increasing tendency compared with that of the corresponding protonated zeolites.

3. 2. Hydrocracking of Phenanthrene

Hydrocracking of phenanthrene over the nickel-supported Y-type zeolite was conducted at 350°C. By changing the time of reaction 0, 15 and 60 min, the recovery of phenanthrene was found to decrease in the order of 80, 16, and 0.7%, respectively (Table 1). The gaseous products in-

creased in the following order, 5.1% (0 min), 15.2% (15 min), and 67.5% (60 min). Plots of the yields of products against reaction time (Fig. 2 based on data of Table 1) indicated that, when the reaction time was 0 min, 9,10-dihydro- and 1,2,3,4-tetrahydrophenanthrenes were produced first, before they were isomerized to five membered saturate rings and skeletally isomerized to *sym*-octahydroanthracene along with the formation of *sym*-octahydrophenanthrene. These compounds decreased after 60 min of reaction due to cracking. After 60 min of reaction, propane, *n*-butane, and *i*-butane became the main gaseous products, in-

Table 2 Results of Hydrocracking for Phenanthrene

Catalyst Concentration of metal species	[wt%]	Ni-Y Ni 3.11	Ni-M Ni 1.77	Ni-ZSM-5 Ni 1.02	S-NiMo/Al ₂ O ₃ Ni 2.8 Mo 13.0
Product distribution	[wt%]				
Gas		67.5	53.8	10.4	0.6
methane			0.1		
ethane		3.2	5.0	5.6	0.3
propane		24.2	33.3	3.1	0.3
i-butane		17.0	8.9	1.3	
n-butane		23.1	6.5	0.4	
Liquid		31.3	26.4	20.6	92.9
Deposited carbon		10.1	3.3	1.2	0.5
Recovery of phenanthrene		0.7	22.3	71.1	0.4
Total ^{a)}		109.6	105.8	103.3	94.4
Hydrogen consumption		16.1	7.9	1.7	6.3
Distribution of liquid products	[wt%]
1.9	33.5	54.2
0.9	3.5	36.1	2.3
1.1	0.6	3.7	50.4
15.0
1.3	1.5
4.5	2.9	1.8	16.8
13.6
0.8	12.8
34.8	18.6		0.5
0.3	3.4
15.0	3.0
27.1	15.9		

a) Total means the sum of wt% of each fraction (liquids, deposited carbons, phenanthrene recovered, and gaseous products). Each fraction has specific error involved in its measurement so normalization to 100% was not used.

dicating that dealkylation reaction had extensively occurred, from 15 min- to 60 min-reaction. One- and two-ring compounds produced were benzene, cyclohexane, tetralin, and indan, along with their alkylated derivatives. At 0 min of reaction, a considerable amount of alkylphenanthrenes was observed; this was probably formed *via* transalkylation between alkylphenanthrene and phenanthrene.

The results of hydrocracking of phenanthrene

using nickel-supported ZSM-5, mordenite and Y-type zeolites are summarized in **Table 2** that shows that catalytic activity of these zeolites increases according to the following order: ZSM-5 (29%) < mordenite (77.7%) < Y-type (99.3%). The number in parentheses indicates the conversion of phenanthrene by hydrocracking. This order agrees well with the increasing order of pore size. Since the size of phenanthrene molecule is reported to be 7.9 Å, it may not be able to enter the channel of neither mordenite nor ZSM-5 type zeolite. On this point, we have conducted simulated diffusion of phenanthrene molecule into the mordenite channel by using the Computer-Aided Molecular Design (CAMD) technique¹⁴⁾. The results indicated that phenanthrene molecule could manage to get into the mordenite channel. Therefore, the reaction using ZSM-5 type zeolite might proceed at outer acid sites. On the other hand, in the case of mordenite and Y-type zeolite, the substrate could enter the channel so that the reaction could proceed effectively to smaller products such as tetralins, indans, and benzenes, in addition to gaseous products. It should be noted that, in the case of mordenite, the yield of 9,10-dihydro-phenanthrene was high and the yields of cyclohexane derivatives were small compared with those with Y-type zeolite. In the case of using protonated Y type catalyst, 70% of phenanthrene was observed along with 6% yield of dihydro- and tetrahydrophenanthrenes and 7% yield of alkylated phenanthrenes, while the yield of gaseous products was less than 5%. These findings in conjunction with the product distribution with Ni-loaded Y-type zeolite clearly indicated that the acid sites in zeolite catalysts did crack hydroaromatic compounds that were supplied by hydrogenation of phenanthrene with the nickel species in the channel of the zeolite.

In the case of using presulfided nickel-molybdenum catalyst (S-NiMo/Al₂O₃), which is often used for upgrading heavy oils, the conversion of the substrate reached 99.6%, and the major products were hydrogenated phenanthrene, anthracene, and benzindan derivatives, and the yields of *sym*-octahydro- and perhydrophenanthrene were 50.4% and 15%, respectively. The above observations indicated that this catalyst, however, did not have the cracking capability.

Other factors affecting the conversion rate of the substrate and distribution of the products are the amount and/or the strengths of the acid sites and the amount of nickel metal in the zeolite. They were increased in the order: ZSM-5 < mordenite < Y-type. This order is similar to that of the size of the zeolite channels as described

in the section on the characterization of catalysts. These observations suggest that the highest activity of Ni-Y catalyst corresponds not only to the size of the channel but also to the number of acid sites and to the concentration of nickel species.

Distribution of liquid products (in **Table 2**) clearly indicated that with runs using ZSM-5 (the smallest pore size), the main products were 9,10-dihydro-, 1,2,3,4-tetrahydro-, and *sym*-octahydro-phenanthrene derivatives along with their isomers (5 membered ring compounds). 9,10- and 1,2,3,4-Positions of phenanthrene can approach the mouth of the channels of ZSM-5 type zeolite, and can take up the hydrogen atoms activated in the channel of the catalyst. Isomerization of naphthenic ring to 5-membered ring seems to take place in the channel of mordenite and Y-type zeolite because this isomerized product can hardly be observed with the ZSM-5 type zeolite. Dihydro-, tetrahydro-, and octahydro-derivatives are not the major products in the case of Y-type zeolite, because they are converted to benzene and cyclohexane derivatives. This difference may not be certain; however, in the mordenite, the same phenomenon takes place except that dihydro-derivative is the main product. These findings clearly suggest that the skeleton of phenanthrene can enter the channel of mordenite and Y-type zeolite as suggested by CAMD study.

To search for the reaction conditions that could suppress the yield of gaseous products but produce mono- and diaromatic compounds in high yields, the following experiments were carried out. First, high loading of nickel seemed to give high yield of gaseous products: it was found that decrease in the amount of nickel loaded in Y-type zeolite (1.33 wt%) resulted in the production of 43.7% liquid product (at 350°C for 60 min), which composed of 42% of tetralins and indans, 20% of benzenes, and 12% of cyclohexanes (based on the yield of liquid products). In the case of using benzene as a solvent, the yield of liquid products was 45.4% and the yields of tetralins and indans, benzenes, and cyclohexanes were 47.8, 24.4, and 11.0%, respectively. The reaction at 325°C for 60 min yielded 49.6% of liquid products, which contained 42.1% of tetralins and indans, 11.1% of benzenes, and 8.7% of cyclohexanes. Second calcium co-loading was considered to increase the cracking ability of nickel-loaded catalysts^{17),18)}, so the run was conducted with a co-loaded (with 0.37 wt% of nickel and 2.37 wt% of calcium) Y-type zeolite with which 59.5% of liquid products could be obtained, and three ring compounds became the main products. These results suggest that it is still difficult to design a reaction capable of

producing mono- and diaromatic hydrocarbons selectively by mere changing of reaction conditions.

3. 3. Pyrene Hydrocracking

In a preceding chapter, it was pointed out that hydrocracking of phenanthrene greatly depended on the pore size of the zeolite. Pyrene's molecular size is 9 Å; therefore, this molecule cannot enter the channel of Y-type zeolite. Since it would be interesting to investigate pyrene cracking with various types of zeolites, the three zeolites were used at 350°C for 0 and 60 min period. **Figure 3** shows the time profile of the yields of the products using Y-type zeolite. At 0 min of reaction time, 4,5-dihydropyrene was obtained as the main product together with two kinds of hexahydropyrenes. In this case, it is interesting to note that 1,2,3,6,7,8-hexahydropyrene was preferred to other isomer and dihydro derivatives, which suggested that 1,2,3-positions of pyrene could approach with ease the channel of Y-zeolite. On the other hand, yields of 4,5,9,10-tetrahydro derivatives were similar to those of two kinds of decahydro-derivatives and perhydro-derivatives, suggesting that production of these kinds of compounds was not preferable because of the steric hindrance between the substrate and the mouth of zeolite channel. As reaction proceeded, the yields of smaller compounds such as one- and two-ring compounds increased significantly while three ring aromatic compounds increased monotonically.

Table 3 shows the results of reaction at 350°C for 60 min using the three zeolites. The conversion rate of pyrene increased in the order: Ni-ZSM-5 < Ni-mordenite < Ni-Y. In the case of using Ni-ZSM-5, a yield of 22.7% of liquid products was obtained, but they were mostly hydrogenated pyrene. With the Ni-loaded mordenite, the yield of liquid products reached 46.1%; however, they contained hydrogenated pyrene as the main product. On the other hand, a yield of 15.3% of smaller compounds such as hexahydro- and dihydrophenarene, acenaphthene, and benzindan was obtained by using Ni-loaded Y-type zeolite. Dihydro-, tetrahydro-, and two kinds of decahydro-pyrenes were obtained as major products by using the Ni-loaded ZSM-5 type catalyst.

3. 4. Combination Use of Two Different Catalysts to Enhance Yields of Mono- and Di-aromatics

Presulfided Ni-Mo catalyst was found very effective for hydrogenation of phenanthrene and pyrene, while Ni-loaded Y-type zeolite was most effective for hydrocracking among the three zeolites. We assumed that partial hydrogenation of polyaromatics over the Ni-Mo catalyst followed

4,5-dihydro- (○), 4,5,9,10-tetrahydro- (●), 1,2,3,3a,4,5-hexahydro- (□), 1,2,3,6,7,8-hexahydro- (■), 1,2,3,3a,4,5,9,10,10a,10b-decahydro- (△), 1,2,3,3a,4,5,5a,6,7,8-decahydro- (▲), perhydro- (+), and alkylated pyrenes (×).

Fig. 3 Time Profile of Production of Hydrogenated Pyrenes

Fig. 4 Distribution of Liquid Products in Single- and Two-stage Hydrocracking Reaction of Pyrene

by cracking over the Ni-loaded Y-type zeolite would exhibit the possibility of yielding more valuable mono- and di-aromatic compounds from pyrene. The results are shown in **Fig. 4**. As described in a previous chapter, neither one- nor two-ring compound was formed in the reaction using presulfided NiMo/Al₂O₃ as catalyst, while the yields of one- and two-ring compounds in the liquid products were 18.8% and 14.0% for Ni-Y, and 8.7 wt% and 8.3 wt% for the combined presulfided NiMo/Al₂O₃ and Ni-Y catalyst, respectively. From these results, it seems difficult to increase the yields of mono- and di-aromatic compounds by use of a combination of two different catalysts for hydrogenation and cracking.

Table 3 The Results of Hydrocracking Reaction of Pyrene by Using Nickel-loaded Zeolites

Catalyst		Ni-Y	Ni-Y	Ni-Y	Ni-M	Ni-ZSM-5	S-NiMo/Al ₂ O ₃
Reaction time	[min]	0	15	60	60	60	60
Product distribution	[wt%]						
Gas		0.3	27.2	31.7	35.7	7.9	5.7
	methane		0.2	0.2			
	ethane		1.9	1.8	1.5	3.0	0.6
	propane	0.2	8.6	10.1	19.4	3.0	2.3
	<i>i</i> -butane	0.1	11.2	12.7	9.1	1.3	1.5
	<i>n</i> -butane		5.3	6.9	5.7	0.6	1.3
Liquids		22.3	36.1	43.0	46.1	22.7	92.3
Deposited carbon		10.7	10.5	10.8	3.0	0.8	1.8
Recovery of pyrene		79.2	21.9	7.3	15.5	67.1	3.5
Total ^{a)}		112.5	95.7	92.8	100.3	98.5	103.3
Hydrogen consumption		7.8	11.4	16.1	12.6	3.6	13.7
Distribution of liquid products
56.5	26.2	10.8	28.4	74.3	5.1
3.0	3.5	2.3	8.1	3.7	1.7
13.5	16.3	9.3	16.0	6.4	14.3
23.8	28.1	15.9	24.5	13.9	25.1
2.9	4.0	5.7		10.2
4.5	5.6	9.3		23.7
0.4	2.8			18.5
1.2	0.8	0.4		
<hr/>
3.2	4.0
3.6	9.0
0.7			
<hr/>
0.3
0.4	1.5			
<hr/>							
Tetralins and Indans			1.2	10.0	0.7		0.5
<hr/>							
Cyclohexanes			1.3	7.7	0.4		
Benzenes			0.1	2.5	5.5		

a) Total means the sum of wt% of each fraction (liquids, deposited carbons, pyrene recovered, and gaseous products). Each fraction has specific error involved in each measurement so normalization to 100% was not used.

4. Conclusion

To develop a reaction for conversion of poly-

aromatics such as phenanthrene and pyrene to mono- and di-aromatic compounds, hydrocracking reaction was conducted by using the three different nickel-loaded zeolite catalysts at 350°C

and for about 1 h. Nickel-loaded Y-type catalyst showed the highest activity among the three zeolite catalysts employed, and almost all phenanthrene was converted. In the case of using Ni-ZSM-5 catalyst which has a smaller pore size of channel compared with that of Y-type zeolite catalyst, the conversion of the substrate decreased substantially, but no mono- and di-aromatics were observed. Based on the channel size of mordenite (7 Å) and that of phenanthrene (7.9 Å), phenanthrene would probably not be able to enter the channel of mordenite; however, the study on diffusion of phenanthrene on mordenite by CAMD technique revealed that the molecule could manage to get into its channel. The fact that product distribution with Ni-mordenite is similar to that with Ni Y-type zeolite, except for some minor differences, is in good agreement with the results of the CAMD study. These results clearly indicate that the pore size of the zeolite channel should be one of the most important factors that determine the degree of hydrocracking of phenanthrene. When pyrene was used as a substrate, a similar tendency of size of the channel influencing the product distribution was observed. Therefore, the conversion of the substrate and the yields of much smaller ring compounds decreased compared with those in the case of phenanthrene. These results indicate that product distribution in hydrocracking of polyaromatic compounds can be evaluated adequately in terms of the relationship between the molecular size of polyaromatics and

the pore size of the zeolite catalyst channel.

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要 旨

3 種のニッケル担持ゼオライト触媒を用いる多環芳香族化合物の水素化分解反応

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細孔径の異なる 3 種のニッケル担持ゼオライト (ZSM-5 型, モルデナイト, Y 型ゼオライト) を触媒に用いたフェナントレンおよびピレンの水素化分解反応を 350°C, 70 kg/cm² の水素加圧下で, 0, 15, 60 分を行った。また, 比較のため予備硫化した Ni-Mo/Al₂O₃ 触媒を用いた反応についても検討を行った。用いたゼオライト触媒により生成物分布は大きく変化することが明らかとなった。フェナントレンを基質とした場合, クラッキング生成物収率はゼオライト触媒の細孔径に依存し, 細孔径の小さい ZSM-5 ゼオライトを触媒とした場合, ジヒドロフェナントレン, テトラヒドロフェナントレン, オクタヒドロフェナントレンの生成が優先した。これは, フェナントレン分子がこのゼオライト触媒の細孔内へ侵入できないためと考えら

れる。一方, Y 型ゼオライトおよびモルデナイトを用いた場合, フェナントレン骨格の分解が効果的に進行し, プロパン, ブタン, ベンゼン類, インダン類が主生成物となった。Ni-Mo/Al₂O₃ 触媒を用いた場合, 基質の水素化が優先し, 分解反応はほとんど進行しなかった。分子サイズが大きく, 3 種のゼオライト細孔内に侵入できないピレンを基質とした場合は部分水素化物が優先して生成する傾向が観測された。また, 単環, 二環化合物への選択的分解を目的として水素化能の高い Ni-Mo/Al₂O₃ 触媒とクラッキング能の高い Ni 担持 Y 型ゼオライトを組み合わせた 2 段階水素化分解についても検討を行った。

Keywords

Zeolite, Hydrocracking, Polycyclic aromatics, Nickel, Pore size, Product distribution