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Effect of modifier Pd metal on hydrocracking of polyaromatic compounds over Ni-loaded Y-type zeolite and its application as hydrodesulfurization catalyst

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Abstract

Hydrocracking of polycyclic aromatics was conducted at 325–350°C for 0 to 1 h under 30–70 kg/cm^2 pressure of hydrogen by using nickel-loaded, palladium-loaded, and nickel- and palladium-co-loaded Y-type zeolite catalysts. The results suggest that Pd-Ni-Y catalyst has the highest activity toward the hydrocracking reaction of phenanthrene and pyrene among the catalysts employed. To enhance the catalytic activity of the Ni-Y catalyst, modifying it with palladium was found to be an effective method. Due to its high hydrocracking ability, the Pd-Ni-Y catalyst was also applied to hydrodesulfurization of dibenzothiophene at 300°C, which results in complete conversion of dibenzothiophene.

Keywords: Hydrocracking; Hydrodesulfurization; Metal-supported zeolite catalyst

1. Introduction

Coal tar obtained from coal carbonization is a treasure of polyaromatic hydrocarbons, where more than 400 kinds of aromatic compounds are found [1]. The content of naphthalene in coal tar is about 9.0%, and it is used as starting materials for phthalic anhydride, dyestuff, pharmaceutical products and synthetic resins [1,2]. On the other hand, phenanthrene and pyrene are also found in coal tar, with contents of about 5.0 and 2.1%, respectively, but they are used only for the production of carbon black and preservatives for timber. Application of these three- or four-ring aromatic compounds for starting materials of fine chemicals has not yet developed extensively [1]. The development of new catalysts which convert these aromatics into mono- or di-aromatic compounds is one of the objectives for utilizing polycyclic aromatics. Hydrocracking of polycyclic aromatic compounds is believed to proceed via formation of the terminal-naphthenic ring of the starting aromatic compounds, followed by cleavage of the naphthenic ring to produce alkylated aromatic compounds which have fewer aromatic rings than the starting aromatics [3–5]. Accordingly, hydrogenation of the aromatic rings and cracking of the resulting naphthenic rings are key steps in the hydrocracking reaction, so that dual functional catalysts such as metal-supported acid catalysts are considered to be the best catalysts [4–12]. Zeolite has controlled pore structures

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and acidity strong enough to crack naphthenic rings. In addition, they can be loaded easily with metal species by ion exchange.

We have studied the hydrocracking of polycyclic aromatic compounds over Ni-loaded zeolite catalysts (ZSM-5, mordenite, and Y-type) and found that the pore size of the zeolite exerts an interesting effect on product distribution [13]. We conducted computer-simulation for diffusion phenomena of the polycyclic aromatic hydrocarbons in the pore of these zeolites and found that the diffusion ability of the substrate strongly affects the product distribution [14]. During these studies, we have found that Ni-loaded Y-type zeolite has the highest activity toward the hydrocracking reaction among the three zeolite catalysts, which is partly due to the fact that the Y-type zeolite has the largest pore size. Recently we found that modifying Ni-loaded Y-type zeolite by Pd-loading enhanced the hydrocracking ability of the catalyst. In this paper, we report the results of both the hydrocracking reaction of phenanthrene (PHEN) and pyrene (PYR), and the hydrodesulfurization of dibenzothiophene (DBT) using Pd-modified Ni-loaded Y-type zeolite.

2. Experimental section

2.1. Preparation of metal-supported zeolites

The NH_4-substituted Y-type zeolite (50 g) was stirred in 1000 ml of an aqueous solution of $Ni(NO_3)_2$ (0.25 M) at 90°C for 96 h, then filtered and dried at 110°C to obtain the nickel cation substituted zeolite. As to the Pd supported one, NH_4-substituted Y-type zeolite (15 g) was treated in an aqueous solution (200 ml) of $[Pd(NH_3)_4](NO_3)_2$ (0.025 M) at 40°C for 24 h. As to Pd-Ni-Y catalysts, NH_4-substituted Y-type zeolite was treated with aqueous $[Pd(NH_3)_4](NO_3)_2$ solution (0.025 M), followed by an aqueous $Ni(NO_3)_2$ solution (0.25 M) as shown in Fig. 1. The resulting cation exchanged zeolites were calcined in a stream of air at 450°C for 4 h, then being reduced in an H_2 atmosphere at 450°C for 1 h. The content of nickel and palladium in each zeolite was determined by using a Rigaku Denki system 3270 type fluorescence X-ray analyzer, the results being summarized in Table 1.

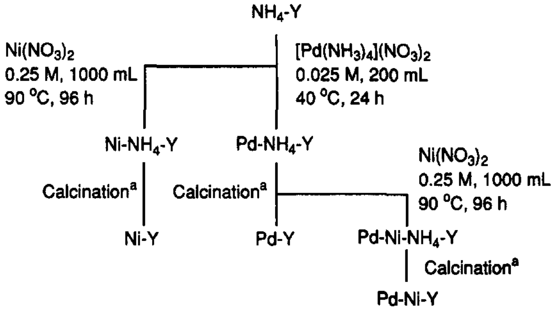

Fig. 1. Preparation of metal cation-exchange zeolite catalysts. [a]At 450°C under air for 4 h, followed by at 450°C under H_2 for 1 h.

2.2. Hydrocracking of PHEN, PYR and DBT

The substrate (1 g) and the catalyst (0.1–0.5 g) were placed in a 70 ml SUS 316 autoclave, which was pressurized to 30–70 kg/cm^2 with hydrogen, then heated up to 300–350°C at the rate of 8°C/min. Reaction time here means the duration at a desired temperature. After the gaseous product was collected, an 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) for quantitative analysis. The liquid product was recovered by washing the inside of the autoclave with CH_2Cl_2. The components of liquid products were identified using a JEOL JMS-DX-303HF type GC–MS, and quantified

Table 1
The catalysts employed in this study

Catalyst	Content (wt%)[a]	
	Ni	Pd
Ni-Y	5.5	
Pd-Y		3.7
Ni-Pd-Y	3.3	3.6

[a]Determined by X-ray fluorescence.

using a Shimadzu GC-14APFSC (CBP-1 capillary column, i.d. 0.5 mm × 25 m). Carbon deposit was defined as the carbonaceous materials remaining on the surface or inside the pore of the catalyst after reaction. The yield was calculated based on the microanalysis of the catalyst recovered.

3. Results and discussion

3.1. Hydrocracking reaction of PHEN

In a previous study, we conducted hydrocracking reaction of PHEN and PYR over three different nickel-supported zeolite catalysts such as nickel-loaded ZSM-5 (Ni-ZSM-5), mordenite (Ni-M), and Y-type zeolite (Ni-Y) at 350°C for 1 h at 70 kg/cm^2 of H_2 and observed that the product distribution depends, to a great extent, on the pore size of zeolite [13]. Conversion of the substrates decreased in decreasing order of pore size and acid sites of the zeolites. By the use of Ni-Y catalyst, which showed the highest activity among the three, PHEN was almost completely converted to gases (mainly propane and butanes, which come from the cleavage of the naphthenic ring) and one- or two-aromatic ring compounds, while considerable amounts of carbonaceous material (about 10 wt%) were formed on the surface of the catalyst. Carbonaceous materials are in general, believed to deactivate catalysts, so it is important to suppress the formation of these materials in the catalytic process. Hydrogenation and hydrogen transfer reactions seem to play a role in suppressing these materials because condensation and polymerization reactions are closely related to the formation of carbonaceous materials. In order to reduce the amount of deposited carbon, we modified the Ni-Y catalyst by loading palladium, since the resulting catalyst is expected to show higher hydrogenating activity than Ni-Y.

We prepared Pd-exchanged Y-type zeolite (Pd-Y) and palladium and nickel co-loaded Y-type zeolite (Pd-Ni-Y) by an ion exchange method from NH_4-Y. The contents of metal species of these catalysts are summarized in Table 1. Using these catalysts, we conducted the hydrocracking reaction of PHEN under the same reaction conditions as reported in the previous paper. The results are summarized in Fig. 2. Yields of gaseous products obeyed the following sequence: Pd-Ni-Y > Pd-Y ≥ Ni-Y. The formation of propane, *i*-butane, and *n*-butane indicates that cleavage of the naphthenic ring

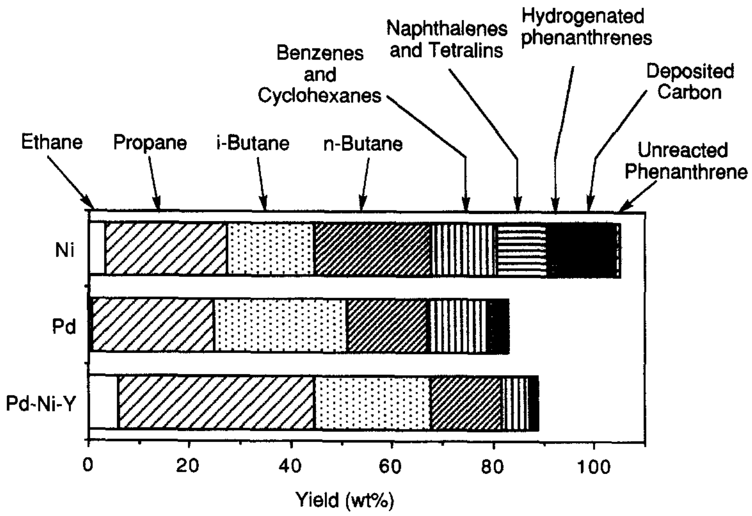

Fig. 2. Hydrocracking of phenanthrene over the metal-supported zeolite catalysts at 350°C for 1 h.

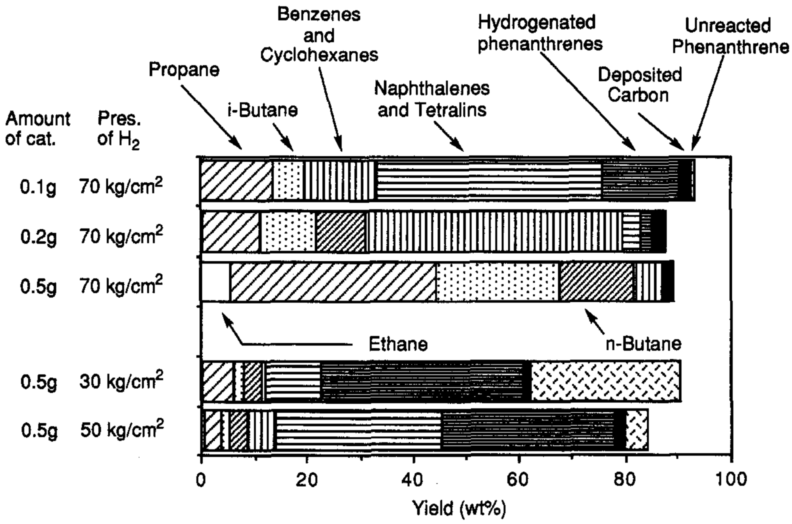

Fig. 3. Hydrocracking of phenanthrene over Pd-Ni-Y catalyst at 350°C for 1 h.

occurred during the above reaction. The yields of coke decreased in the order Ni-Y > Pd-Y > Pd-Ni-Y. These results suggest that the extent of suppressing coke formation strongly depends on the hydrogenating ability of the catalysts.

To obtain one- and two-ring compounds in high yields, the PHEN hydrocracking reaction was conducted under milder reaction conditions. Decreasing the pressure of H_2 (from 70 to 30 or 50 kg/cm^2) resulted in a decrease of cracked products (Fig. 3). When using 0.1 g of Pd-Ni-Y with 1 g of PHEN at 350°C for 1 h under 70 kg/cm^2 of H_2, two-ring compounds, derivatives of naphthalene and tetralin, were the main products (43% yield), while benzenes and cyclohexanes were obtained as main products (49% yield) when using 0.2 g of Pd-Ni-Y (Fig. 3) under similar reaction conditions. These re-

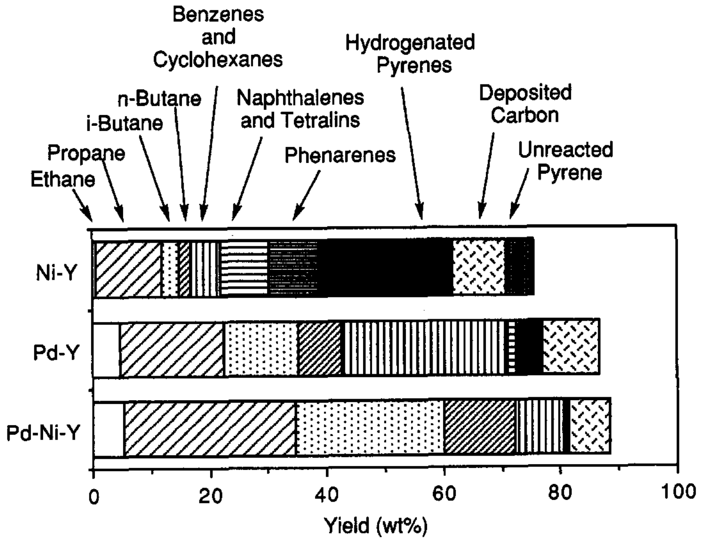

Fig. 4. Hydrocracking of pyrene over the metal-supported zeolite catalysts at 350°C for 1 h.

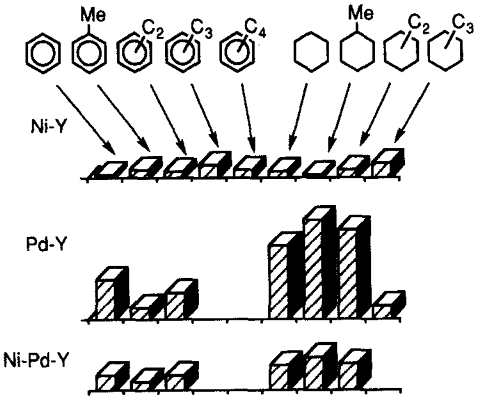

Fig. 5. Distribution of one-ring compounds in hydrocracking of pyrene over three metal-supported Y-type zeolite catalysts at 350°C for 1 h under 70 kg/cm^2 of H_2.

sults suggest that, at 350°C for 1 h, efficient hydrocracking of PHEN needs a higher pressure of H_2, and at 70 kg/cm^2 of H_2, the amount of catalysts employed could control product distribution and afford either one- or two-ring compounds in relatively high yield.

3.2. Hydrocracking reaction of PYR

As described in a previous paper, we have carried out Ni-Y catalyzed hydrocracking of PYR [13]. However, 5% PYR remains unreacted and hydrogenated pyrenes were as high as 23%. This results could be interpreted by the fact that the pore size of Y-type zeolite is somewhat smaller than the molecular size of PYR. In order to improve the activity of Ni-Y catalyst, we prepared a Pd-Ni-Y catalyst. It is interesting to examine the hydrocracking of PYR over this catalyst.Using three different catalysts, Ni-Y, Pd-Y, and Pd-Ni-Y, hydrocracking of PYR was conducted, and the results are shown in Fig. 4. In the presence of Pd-Y or Pd-Ni-Y catalyst, PYR was almost completely converted to gases (C_2, C_3, i-C_4, n-C_4) and derivatives of benzene or cyclohexane along with carbon deposited on the catalyst surface. In the run using Pd-Ni-Y catalyst, the yield of gases reached

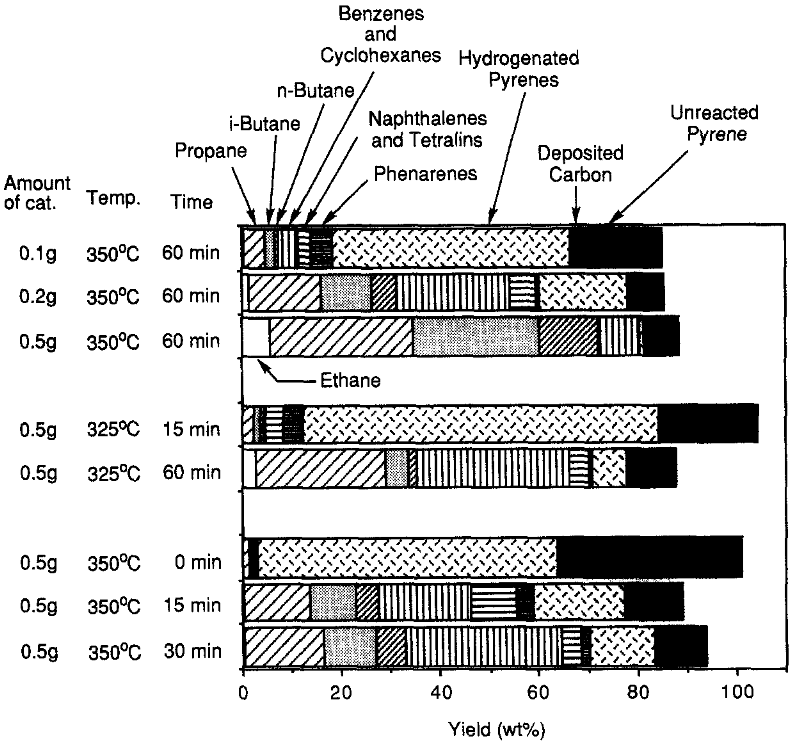

Fig. 6. Hydrocracking of pyrene over Pd-Ni-Y catalyst.

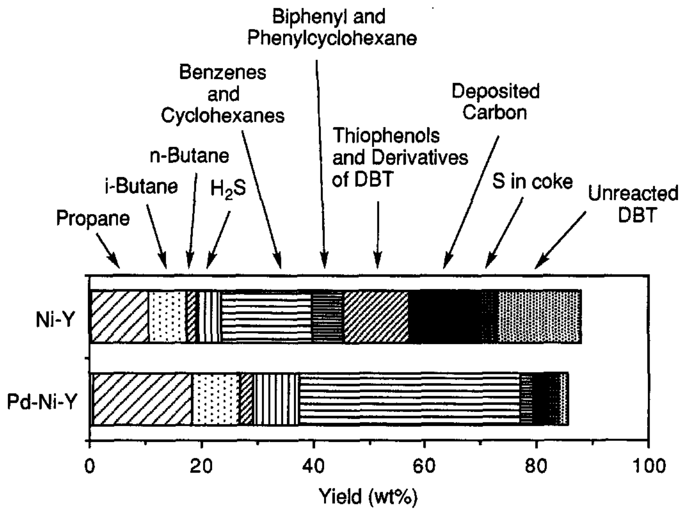

Fig. 7. Hydrodesulfurization of dibenzothiophene over the metal-supported zeolite catalysts at 300°C for 1 h.

70%. The amounts of carbon deposited on the catalyst were 9.1% for Ni-Y, 9.6% for Pd-Y, and 7.0% for Pd-Ni-Y catalyst. On the basis of the high yields of gaseous products and considerable coke formation, it appears that cracking reactions occurred in preference to hydrogenation. Fig. 5 summarizes the distribution of 1-ring compounds produced from hydrocracking of PYR over the three catalysts. In the run using Ni-Y catalyst, there was no selective formation of any compound relative to the other products. In the runs with Pd-Y and Pd-Ni-Y catalysts, the yield of cyclohexanes was higher than that of benzenes. No C_3- and C_4-benzenes and C_3-cyclohexanes were observed in the products obtained from the reaction using Pd-Ni-Y catalyst. These results indicated that activity of Pd-Ni-Y catalyst toward hydrogenation and cracking reaction is the highest among the three catalysts. There are two possibilities for this high activity of Pd-Ni-Y in the case of the pyrene molecule which cannot enter into the cage of the Y-type zeolite. First, Pd species enhance not only the hydrogenating ability of Ni-Y but also the cracking activity. Second, Pd species only enhance the hydrogenating ability of Ni-Y but the resulting hydrogenated pyrenes are more flexible sterically than the starting materials, so that the hydrogenated substrate can enter into the pores of the catalyst with ease. Now, we do not have enough data to determine which is the more plausible for the high activity attained by Pd-Ni-Y. We are now conducting a computer simulation study of diffusion phenomena of hydrogenated aromatic hydrocarbons in the pores of zeolite [1].

Fig. 6 shows the effects of amount of catalyst employed on the product distribution. In the case using 0.1 g of Pd-Ni-Y, hydrogenated pyrenes were still the main products (48%). However, increasing the amount of the catalyst (from 0.1 to 0.2 g) led to drastic changes in product distribution (Fig. 6). These results also suggest that the product distribution can be changed, but selectivity can hardly be controlled by changing the amount of the catalyst (at least not in the same way as the selectivity of PHEN hydrocracking could be controlled by changing the catalyst loading). So we further examined the effects of reaction temperature and duration on the product distribution (Fig. 6). In the reac-

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[1] After submission of the present paper, we carried out a CAMD study to examine the second possibility. The results suggest that hydrogenated pyrenes, 4,5-dihydro- and 4,5,9,10-tetrahydropyrenes, could hardly move in the channels of a Y-type zeolite. Therefore, we now consider that first possibility is more plausible. This discussion will be published in the next paper.

tion at 350°C for 0 min (the reactor was quenched immediately after heating up to the reaction temperature), 25% of PYR still remained unreacted and the main products were hydrogenated pyrenes (61%). After 30 min at 350°C, no PYR was recovered and gases and one-ring compounds (32%) became the main products. In the reaction at 325°C for 60 min, a similar product distribution to that in the reaction at 350°C for 30 min was attained. These results suggested that the product distribution could be controlled in a more effective way by changing the reaction temperature and duration (relative to the change of catalyst loading), especially in the case of pyrene.

3.3. Hydrodesulfurization of dibenzothiophene

In the experiments of hydrocracking of polycyclic aromatics such as phenanthrene or pyrene, we found that Pd-modified Ni-Y catalyst showed a very high activity for hydrogenation and hydrocracking. So, we tried to apply this modified catalyst for the hydrodesulfurization of DBT. DBT is currently considered to be one of the best model compounds for the hydrodesulfurization reaction. The reaction was conducted at 300°C for 1 h under 70 kg/cm^2 of H_2 using Ni-Y and Pd-Ni-Y catalysts (0.5 g). The results are shown in Fig. 7. In the case using Ni-Y catalyst, 12% of DBT remained unreacted, and there were 12% sulfur-containing compounds in the products. In the run using Pd-Ni-Y catalyst, DBT was almost completely converted into gases (C_3, i-C_4, and n-C_4) and one-ring compounds, and no sulfur-containing compound was detected in the liquid products. These results suggest that Pd-Ni-Y catalyst is effective for the hydrodesulfurization of DBT. A further detailed study is now under consideration.

4. Conclusion

In order to enhance the catalytic activity of nickel-loaded Y-type zeolite catalyst toward hydrocracking of polyaromatics and hydrodesulfurization of dibenzothiophene, we modified it by palladium-loading and examined the activity of the resulting catalyst. In the case of phenanthrene hydrocracking, we found that the amount of the catalyst employed could control the product distribution: in the run using 0.2 g of Pd-Ni-Y at 350°C under 70 kg/cm^2 of H_2 for 1 h, one-ring compounds were obtained as major products, while the reaction with 0.1 g of the catalyst afforded two-ring compounds in relatively high yields. With respect to the pyrene, changing the reaction temperature and/or duration in the runs with 0.5 g of the catalyst was found to be more effective than changing the amount of catalyst. Using Pd-Ni-Y, complete conversion of dibenzothiophene could be attained at 300°C for 1 h. These results clearly indicate that palladium loading is an effective method to enhance the catalytic activity of nickel-loaded Y-type zeolite catalyst.

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