

EFFECT OF MODIFIER Pd METAL ON HYDROCRACKING OF POLYAROMATIC COMPOUNDS OVER Ni-LOADED Y-TYPE ZEOLITE AND ITS APPLICATION AS HYDRODESULFURIZATION CATALYSTS

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INTRODUCTION

Coal tar obtained from coal carbonization is a treasure of polyaromatic hydrocarbons, where more than 400 kinds of aromatic compounds are found to be contained. Naphthalene's content in coal tar is about 9.0 %, being used as starting materials for phthalic anhydride, dye stuff, pharmaceutical products and synthetic resins. On the other hands, phenanthrene and pyrene are contained in the yield of 5.0 % and 2.1 %, respectively, being used only for production of carbon black and antiseptics of timbers. Application of these three or four ring aromatic compounds for starting materials of fine chemicals is not yet developed so extensively. The development of new catalysts being able to convert these aromatics into mono or diaromatic compounds is one of objectives for utilization of polyaromatics. Hydrocracking of polyaromatic compounds is believed to proceed via formation of terminal-naphthenic ring of starting aromatic compounds, followed by cleavage of the naphthenic ring to produce alkylated aromatic compounds which has less numbers of ring than starting aromatics. Accordingly, hydrogenation of aromatic rings and cracking of resulting naphthenic rings are key steps of hydrocracking reaction, so that dual functional catalysts such as metal-supported acid catalysts are considered to be one of the best catalysts.^{1,2} Zeolite has controlled pore structures and strong acidity enough to crack naphthenic rings, being characteristics in exchanging metal species with ease. We have been studying the hydrocracking of polyaromatic compounds over Ni-loaded zeolite catalysts (ZSM-5, mordenite, and Y-type) and found the fact that pore size of zeolite exerts an interesting effect on product distribution.³ We also conducted computer-simulation for diffusion phenomena of the polyaromatic hydrocarbons in the pore of these zeolites and found that diffusion ability of the substrate affects strongly the product distribution.³ Recently we found that modifying of Ni-loaded Y-type zeolite by Pd-loading enhanced hydrocracking ability of the catalyst. In this report, we would like to refer to the results of both hydrocracking reaction of pyrene and hydrodesulfurization of dibenzothiophene using Pd-modified Ni-loaded Y-type zeolite.

Experimental Section

Preparation of metal-supported zeolites

The NH_4 -substituted Y-type zeolite (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 being filtered and dried at 110 °C to obtain the nickel cation substituted zeolites. As to the Pd supported one, NH_4 -substituted Y-type zeolite (15 g) was treated in aqueous solution (200 ml) of $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$ (0.025 M) at 40 °C for 24 h. As to Ni-Pd-Y catalysts, NH_4 -substituted Y-type zeolite was treated with aqueous $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$ solution, followed by aqueous $\text{Ni}(\text{NO}_3)_2$ solution. The resulting cation exchanged zeolites were calcined in a stream of air at 500 °C for 4 h, being submitted to the reduction with 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, this being summarized in Table 1.

Hydrotreatment of pyrene or dibenzothiophene

The substrate (1 g) and the catalyst (0.5 g) were placed in a 70 ml SUS 316 autoclave, which were pressurized to 70 kg/cm² with hydrogen, being followed by heating up to 350 °C with the rate of 8 °C / min. Reaction time is the duration being kept at 350 °C. 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 the inside of the autoclave with CH_2Cl_2 . According to the analysis by a JEOL JMS-DX-303HF type GC-MS, components of liquid products were assigned, their quantitative analyses being conducted by a Shimadzu GC-14APFSC (CBP-1 capillary column, f 0.5 mm x 25 m). The carbon deposited on the catalyst was calculated based on the microanalysis of the recovered catalyst.

Results and Discussion

Hydrocracking reaction of pyrene

In a previous study, we conducted hydrocracking reaction of phenanthrene and pyrene over three

different Ni-supported zeolite catalysts such as Ni-loaded ZSM-5, mordenite, and Y-type zeolite at 350 °C for 1 h at 70 kg/cm² of hydrogen and found that pore size of zeolites is controlling product distribution. Conversion of the substrates depended also on the size of these zeolites. By the use of Ni-loaded Y-type zeolite (Ni-Y) catalyst, phenanthrene was completely converted to gases and one- or two-ring compounds, while in the case of pyrene both hydrogenated pyrene and unreacted one still remained in the product. This results could be interpreted by the fact that the pore size of Y-type zeolite is larger than the molecular size of phenanthrene, however, it is somewhat smaller than that of pyrene. In order to improve the activity of Ni-Y catalyst, we examined modifying of Ni-Y catalyst by loading second metal species.

We prepared Pd-modified Ni-Y (Ni-Pd-Y) catalyst by ion exchange of NH₄-substituted Y-type zeolite with aqueous [Pd(NH₃)₄]²⁺ solution followed by Ni²⁺ solution. Concentration of metal species on the resulting zeolite is summarized in Table 1. To examine catalytic activity of Pd metal itself, we also prepared Pd-loaded Y-type (Pd-Y) zeolite. Using these three catalysts, hydrocracking of pyrene was conducted in a 70 mL autoclave at 350 °C for 1 h at 70 kg/cm² of hydrogen, the results being shown in Figure 1. In the presence of Pd-Y or Ni-Pd-Y catalyst, pyrene was completely converted to gases (from methane to butane) and derivatives of benzene or cyclohexane, especially in the case using Ni-Pd-Y catalyst, yield of gases reached to 70%. Amounts of carbon deposited on the catalyst were 9.1% for Ni-Y, 9.6% for Pd-Y, and 7.0% for Ni-Pd-Y catalyst. Figure 2 summarizes the distribution of mono-ring compounds produced from hydrocracking of pyrene over three catalysts. In the case using Ni-Y catalyst, the selective formation of each compound was not observed, while, the yield of cyclohexanes was higher than that of benzenes in the case using Pd-Y and Ni-Pd-Y catalysts. No C₇- and C₈-benzenes and C₇-cyclohexanes was observed in products obtained from the reaction using Ni-Pd-Y catalyst. These results indicated that activity of Ni-Pd-Y catalyst toward hydrogenation and cracking reaction is the highest among three catalysts. This finding agrees well with the fact that the ratio of *i*-butane to *n*-butane (2.1) of gaseous products in the reaction using Ni-Pd-Y catalyst was slightly higher than that (1.8) from the reaction using Ni-Y catalyst. This higher activity of Ni-Pd-Y catalyst might be partly due to the decrease of carbon deposited on the catalyst, this often leading to deactivation of the catalyst.

Effects of reaction temperature and duration on the extent of hydrocracking were also investigated, the results being shown in Figure 3. In the reaction at 350 °C for 0 min, 25% of pyrene was still remained and main products were hydrogenated pyrenes (60%). With the reaction time being longer than 30 min, no pyrene was recovered and gases and mono-ring compounds became main products. In the reaction at lower temperature such as 325 °C, conversion of pyrene was still higher than that in the reaction using Ni-Y catalyst at 350 °C. These results suggested that modifying of Ni-Y catalyst by Pd can reduce the reaction temperature of hydrocracking of pyrene compared with Ni-Y catalyst.

Hydrodesulfurization of dibenzothiophene

In a previous chapter, we found that modifying of Ni-Y catalyst by Pd-loading resulted in very high activity for hydrogenation or hydrocracking of polyaromatic hydrocarbons. So, we tried to apply this modified catalyst for hydrodesulfurization (HDS) of dibenzothiophene (DBT). HDS reaction of DBT was conducted at 300 °C for 1 h under 70 kg/cm² of H₂. Figure 4 shows the product distribution of HDS reaction by using Ni-Y and Ni-Pd-Y catalysts. In the case using Ni-Y catalyst, 15% of DBT was recovered along with 12% yield of sulfur-containing compounds, while, using Ni-Pd-Y catalyst, DBT was almost converted to gases and monoring compounds and no sulfur-containing compound was observed in the liquid products. These results suggest that high activity of Ni-Pd-Y catalyst is much more effective for HDS reaction. Now, we are conducting characterization of this active catalyst.

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4. REFERENCES

- 1) Hayes Jr., H. W.; Parcher, J. F.; Halmer, N. E. *Ind. Eng. Chem. Process Des. Dev.*, **1983**, *22*, 401.
- 2) Lapinas, A. T.; Klein, M. T.; Gates, B. C.; Macris, A.; Lyons, J. E. *Ind. Eng. Chem. Res.*, **1987**, *26*, 1026.
- 3) Matsui, H.; Akagi, K.; Murata, S.; Nomura, M. *Jpn. Petrol. Inst., in contribution*.
- 4) Matsui, H.; Akagi, K.; Murata, S.; Nomura, M. *Energy Fuels*, *in press*.

Table 1. The catalyst employed in this study

	Contents (wt%)	
	Ni	Pd
Ni-Y	5.5	-
Ni-Pd-Y	3.3	3.6
Pd-Y	-	3.7

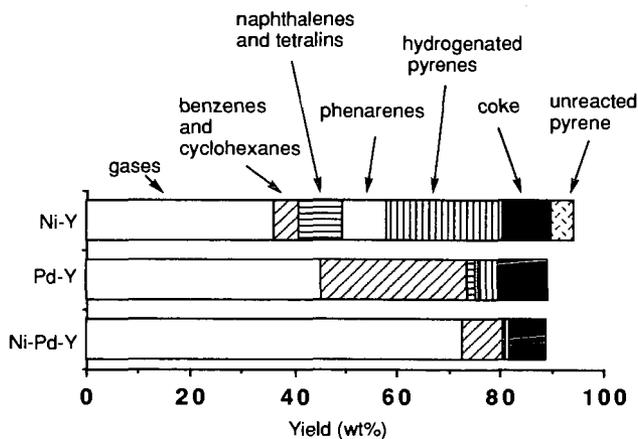


Figure 1. Hydrocracking of pyrene over metal-supported Y-type zeolites at 350 °C for 1h

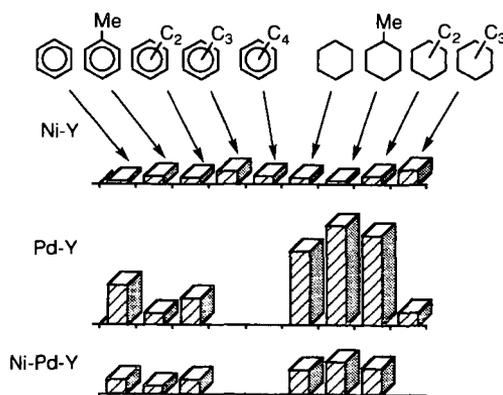


Figure 2. Distribution of mono-ring compounds in hydrocracking of pyrene over three metal-supported Y-type zeolite catalysts at 350 °C for 1 h under 70 kg/cm² of H₂

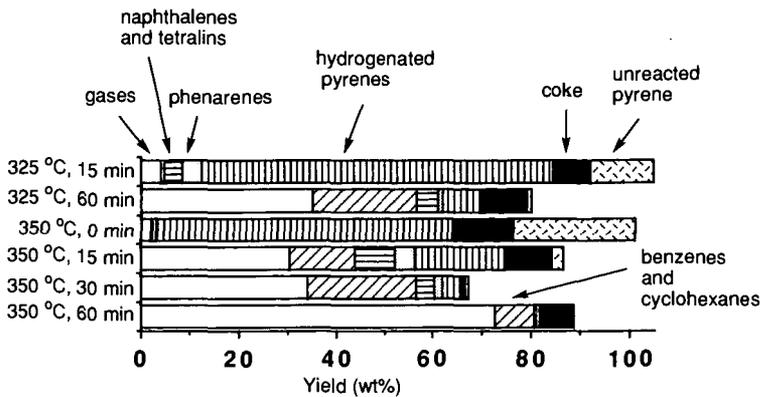


Figure 3. Hydrocracking of pyrene over Ni-Pd-Y catalyst

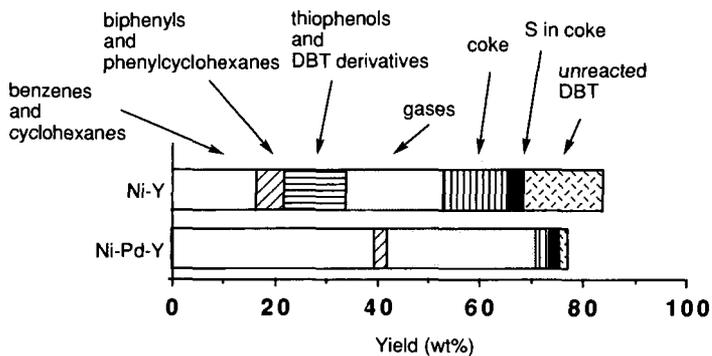


Figure 4. Hydrodesulfurization of DBT over metal-supported Y-type zeolite at 350 °C for 1h