Effective Hydrocracking of 4,6-Dimethyldibenzothiophene Catalyzed by Palladium- and Nickel-Co-Loaded Y-type Zeolite

Kazuyoshi Kaneda, Takema Wada, Satoru Murata, and Masakatsu Nomura*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565

(Received May 23, 1996)

Palladium- and nickel-co-loaded Y-type zeolite was examined for the catalyst of hydrocracking of 4,6-dimethyldibenzothiophene at 320-340 °C for 1-2 h under 70 kg/cm^2 of an H_2 pressure. Under the conditions, 4,6-dimethyldibenzothiophene was almost completely converted to gases (C_2-C_4), benzene and cyclohexane derivatives, and H_2S.

Hydrodesulfurization is one of the most important processes for upgrading of heavy oils. Therefore, numerous studies were extensively conducted. Recently, these studies have been focused on deep desulfurization of gasoil required by the current regulation. Generally, it is well known that dibenzothiophene (DBT) is one of the sulfur-containing model compounds which tends to show high resistivity toward deep HDS. Therefore, DBT becomes a typical target molecule.[1-4]

In a recent study, we investigated hydrocracking (HC) reaction of dibenzothiophene catalyzed by metal-loaded zeolites and found that palladium- and nickel-co-loaded Y-type (Pd-Ni-H-Y) zeolite has the highest activity among the catalyst examined (Ni-H-Y, Pd-H-Y, and Pd-Ni-H-Y).[5] In the present study, we would like to report the results of HC reaction of 4,6-dimethyldibenzothiophene (DMDBT), which is known as a tougher compound for desulfurization than DBT.[6-8]

The Pd-Ni-H-Y catalyst, employed in this study, was prepared by ion-exchange method from NH_4-substitued Y-type zeolite (Shokubai Kasei Co. Ltd., NH_4-Y powder No. 23650) with $[Pd(NH_3)_4](NO_3)_2$, followed by $Ni(NO_3)_2$ aqueous solution. Before the reaction, the resulting Pd-Ni-NH_4-Y type catalyst was calcined at 450 °C for 4 h under an air stream and reduced at the same temperature for 1 h under a hydrogen stream. Contents of nickel and palladium in the catalyst were 3.3 and 3.6 wt%, respectively, by X-ray fluorescence. HC reaction of DBT or DMDBT was conducted according to the following method: substrate (1 g) and the catalyst (0.5 g) were placed in a 70 ml SUS 316 autoclave, which was pressurized to 70 kg/cm^2 with hydrogen, and then heated up to a desired temperature (320-340 °C) at the rate of 8 °C / min. Reaction time here means the duration at reaction temperature. After the end of the reaction, the liquid products were recovered by washing the inside of the apparatus with CH_2Cl_2 and analyzed by a Shimadzu GC-14APFSC gas chromatograph and a JEOL JMS-DX-303 GC-MS.

The results for hydrocracking reaction of DMDBT are displayed in Figure 1 along with that of DBT. In the reaction of DBT at 320 °C for 1 h under 70 kg/cm^2 of H_2 (the optimized conditions for the reaction of DBT), it was almost completely converted to gaseous products and the derivatives of benzene and cyclohexane. On the other hand, in the reaction of DMDBT at 320 °C for 1h, its conversion reached 98%, while hydrogenated DMDBT derivatives and the other sulfur-containing compounds still remained. Either elongation of reaction duration to 2 h or increase of reaction temperature to 340 °C resulted in almost complete conversion of DMDBT and no sulfur containing-compounds are observed in the products. In these conditions, H_2S was obtained in 13-15% yield, which corresponded to 82-94% of sulfur contained in DMDBT. These results clearly indicate that palladium- and nickel-co-loaded Y-type zeolite could crack not only DBT but also DMDBT to a great extent. As to hydrodesulfurization of alkyldibenzothiophenes, several studies were conducted by using Ni-Mo/Al_2O_3 or Co-Mo/Al_2O_3,[6-8] where main products were alkylated biphenyls and their hydrogenated derivatives. In our case, major products were C_2-C_4 hydrocarbons and derivatives of benzene and cyclohexane. These differences may be caused by the strong acidity generated from co-loading of palladium and nickel. Further investigation including detailed analysis of the products and control of catalyst acidity by metal loading is now in progress.

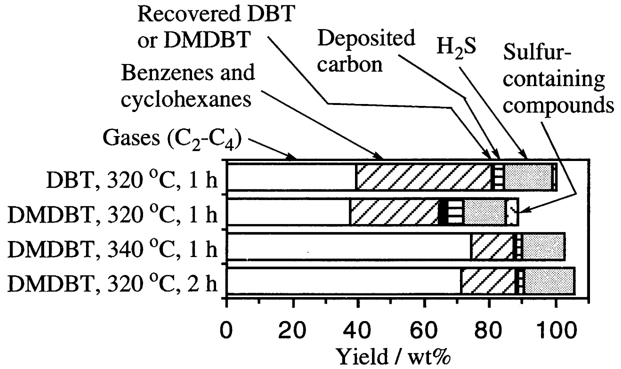

Figure 1. Hydrodesulfurization of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) in the presence of Pd-Ni-H-Y catalyst under 70 kg/cm^2 of H_2.

This work was supported by Grant-in-Aid for Scientific Research No. 07242249 from the Ministry of Education, Science and Culture, Japan.

References

1 T. Kabe, W. Qian, and A. Ishihara, *J. Catal.*, **149**, 171 (1994).
2 X. Ma, K. Sakanishi, T. Isoda, and I. Mochida, *Energy Fuels*, **9**, 33 (1995).
3 C. W. Curtis, J. H. Chen, and Y. Tang, *Energy Fuels*, **9**, 195 (1995).
4 C. Bianchini, J. A. Casares, M. V. Jimenez, A. Meli, S. Moneti, F. Vizza, V. Herrera, and R. Sanchez-Delgado, *Organometallics*, **14**, 4850 (1995).
5 T. Wada, K. Kaneda, S. Murata, and M. Nomura, *Catal. Today, in press.*
6 D. R. Kilanowski, H. Teeuwen, V. H. J. de Beer, B. C. Gates, G. C. A. Schuit, and H. Kwart, *J. Catal.*, **55**, 129 (1978).
8 A. Ishihara, H. Tajima, and T. Kabe, *Chem. Lett.*, **1992**, 669; T. Kabe, A. Ishihara, and Q. Zhang, *Appl. Catal., A: Gen.*, **97**, L1 (1993).
8 T. Isoda, X. Ma, and I. Mochida, *Sekiyu Gakkaishi*, **37**, 368 (1994); T. Isoda, S. Nagao, X. Ma, Y. Korai, and I. Mochida, *Energy Fuels*, **10**, 482 (1996).