[Letter]

Aromatic Hydrogenation of Distillate over B_2O_3 - Al_2O_3 Supported Pt-Pd Catalysts

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The potential of B_2O_3 - Al_2O_3 -supported bimetallic Pt-Pd catalysts for aromatic hydrogenation of distillate was investigated. The activity measurements were carried out with hydrotreated light cycle oil (LCO)/straight-run light gas oil (SRLGO) feed containing 33 vol% aromatics and 320 ppm sulfur under practical conditions. As a result, it appeared that Pt-Pd/ B_2O_3 - Al_2O_3 catalysts have much higher activity for aromatic hydrogenation as compared to Pt-Pd/ Al_2O_3 catalysts.

1. Introduction

High aromatics content in diesel fuel lowers fuel quality and has been recognized to bring about the formation of undesirable emissions in exhaust gases from diesel engines ¹⁾. As a result of the gradual change to more stringent environmental regulations, much attention has been paid to the deep reduction of aromatics in middle distillates. To achieve the deep aromatic hydrogenation, two different methods, that is, single-stage and two-stage hydrotreating processes have been proposed ^{2), 3)}. The single-stage hydrotreating process using conventional hydrodesulfurization (HDS) catalysts (CoMo, NiMo, and NiW on Al_2O_3) can only work under severe operating conditions, such as much higher hydrogen pressure and higher temperature. However, because the aromatic hydrogenation is exothermic reaction, there are thermodynamic equilibrium limitations at high temperature operation. On the other hand, the two-stage hydrotreating process using noble-metal catalysts in the second stage can achieve deep levels of aromatic hydrogenation under mild operating conditions, such as moderate hydrogen pressure and lower temperature. However, because noble-metal catalysts are readily poisoned by small amounts of sulfur, the HDS catalyst in the first-stage reactor has to reduce the level of sulfur up to a few ppm. The two-stage hydrotreating process using noble-metal catalysts in the second stage can achieve deep levels of aromatic hydrogenation under mild operating conditions. Therefore, extensive studies have been carried out to develop sulfur-tolerant noble-metal catalysts for the two-stage process by many researchers ^{2)~5)}. In particular, zeolite-supported noble-metal (Pt and/or Pd) catalysts have been receiving more attention as aromatic hydrogenation catalysts. The purpose of this work is to develop a sulfur-tolerant noble-metal catalyst with significantly increased catalytic activity for aromatic hydrogenation. Particularly, to suppress the cracking activity, we have focused on the application of amorphous acidic support, B_2O_3 - Al_2O_3 , which indicates weaker acidity than zeolites.

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2. Experimental

Monometallic and bimetallic Pt and Pd catalysts were prepared by pore volume impregnation on supports (Al_2O_3 : 380 m^2/g and B_2O_3 (10 mass%)- Al_2O_3 : 374 m^2/g), using an aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ and PdCl_2 as the impregnating salt, in the presence of dilute hydrochloric acid. After impregnation these catalysts were dried and calcined in air at 773 K for 4 h. Prior to the activity tests, fresh catalysts were reduced in an H_2 flow at 623 K for 2 hours. Feedstock for this work was prepared by mixing LCO and SRLGO. The mixing ratio of LCO/SRLGO in the feed oil was 30 vol%/70 vol%. Because noble-metal catalysts are used in the latter reactor of the two-stage hydrotreating process, the LCO/SRLGO feed was previously hydrotreated using a HDS catalyst (C-603A⁶⁾ of Cosmo Oil Co.). The general properties of the untreated and hydrotreated LCO/SRLGO are given in **Table 1**. Hydrogenation runs were carried out with the micro-catalytic reactor. Hydrogenation of hydrotreated LCO/SRLGO feed was carried out under the following conditions: temperature, 573 K; total pressure, 4.9 MPa; liquid hourly space velocity (LHSV), 1.5 h^{-1} ; hydrogen-to-feed oil ratio, 500 Nl/l . The percentage and type of aromatics content in feed and products were measured by high-performance liquid chromatography (HPLC) (UV-8200, RI-8200, Tosoh Co.). The decrease in the total aromatics content in distillates was assumed to be pseudo-first-order³⁾. The surface acidity of Al_2O_3 and B_2O_3 - Al_2O_3 was investigated using the temperature-programmed desorption of ammonia (NH_3 -TPD) (TPD-I-AT, Bel Japan).

Table 1 Feed Properties of Untreated LCO/SRLGO and Hydrotreated LCO/SRLGO

	LCO/ SRLGO	Hydrotreated LCO/SRLGO
Sulfur, massppm	1.0×10^4	320
Nitrogen, massppm	200	26
Density(15°C), g/cm^3	0.8713	0.8450
Paraffins, vol%	55.9	67.2
Olefins, vol%	4.2	0.0
Total aromatics, vol%	40.0	32.8
Mono-, vol%	20.5	29.1
Di-, vol%	17.3	3.5
Tri-, vol%	2.2	0.1
Distillation		
IBP, °C	171.5	176.5
50%, °C	298.0	290.5
FBP, °C	387.0	381.5

3. Results and Discussion

The activity measurements of $\text{Pt}(0.5 \text{ mass\%})/\text{Al}_2\text{O}_3$ and $\text{Pt}(0.5 \text{ mass\%})/\text{B}_2\text{O}_3(10 \text{ mass\%})-\text{Al}_2\text{O}_3$ were carried out with hydrotreated LCO/SRLGO (320 ppm sulfur). The first-order rate constants for the catalysts are shown in **Table 2**. It is shown that the activity of $\text{Pt}/\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ is much higher than $\text{Pt}/\text{Al}_2\text{O}_3$. It is clearly demonstrated

that the $\text{B}_2\text{O}_3\text{-Al}_2\text{O}_3$ support has a highly beneficial effect on the Pt metal phase. This enhancement of the activity may be explained by the nature of the support and particularly by the increase in the acidity following the sequence $\text{Al}_2\text{O}_3 < \text{B}_2\text{O}_3\text{-Al}_2\text{O}_3$ (Table 2).

Table 2 The First-order Reaction Rate Constants for the Aromatic Hydrogenation over $\text{Pt/Al}_2\text{O}_3$ and $\text{Pt/B}_2\text{O}_3\text{-Al}_2\text{O}_3$ Catalysts (reaction time, 8 days)

Catalyst	Amount of acidity on support, mmol/g	Aromatics content in product, %	First-order reaction rate constant
$\text{Pt(0.5)/Al}_2\text{O}_3$	0.57	30.0	0.13
$\text{Pt(0.5)/B}_2\text{O}_3(10)\text{-Al}_2\text{O}_3$	0.90	17.0	0.99

It has been reported in the literature ^{7,8)} that, on acidic supports, electron-deficient noble-metal clusters may be formed which possess different catalytic properties. The electron deficiency weakens the metal-sulfur bonding, thus improving the sulfur tolerance of the catalyst. Therefore, it is assumed that the acidity of the $\text{B}_2\text{O}_3\text{-Al}_2\text{O}_3$ support improved the sulfur tolerance of the Pt active metal phase.

Next, to investigate the effect of Pd loading on the hydrogenation activity, we examined the hydrogenation rate constants as a function of Pd loading of the $\text{Pt-Pd/B}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Pt-Pd/Al}_2\text{O}_3$ catalysts. For all catalysts, the Pt loading was held constant at 0.5 mass% as the Pd concentration was varied. The activity measurements were carried out with hydrotreated LCO/SRLGO (320 ppm sulfur) at 573 K and a hydrogen pressure of 4.9 MPa. The effect of Pd loading over the $\text{Pt-Pd/B}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Pt-Pd/Al}_2\text{O}_3$ catalysts is shown in Figs. 1A, B. Fig. 1A indicates that aromatics content in product as a function of Pd content. Aromatics content decreases significantly with Pd content. Particularly, in the case of $\text{Pt(0.5 mass\%)-Pd(0.93 mass\%)/B}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst, it is possible to achieve ultra-deep aromatic reduction (less than 5 vol% aromatics). Also, as shown in Fig. 1B, the hydrogenation

Fig. 1 The Effect of Pd Loading over $\text{Pt-Pd/B}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Pt-Pd/Al}_2\text{O}_3$. (A) Pd Concentration vs. Aromatics Content, (B) Pd Concentration vs. Rate Constant (reaction time, 8 days)

first-order rate constants for the catalysts increased linearly with the Pd content. From the results, it is assumed that there is an interaction of Pt and Pd in the Pt-Pd/B₂O₃-Al₂O₃ catalysts and it improves the hydrogenation activity of aromatics in distillates containing sulfur compounds. Also, in the case of the Al₂O₃ support, like the B₂O₃-Al₂O₃ support, the hydrogenation activity was improved linearly as the Pd content increased. In agreement with our work, Chang *et al.*⁹⁾ previously reported that the addition of Pd to the Pt/Al₂O₃ catalyst significantly improves the activity for aromatic hydrogenation. However, as shown in **Figs. 1A, B**, when the quantity of Pd is identical, the hydrogenation activity of Pt-Pd/B₂O₃-Al₂O₃ catalyst is much higher than that of Pt-Pd/Al₂O₃ catalyst. It seems that the compound effect of the support plays some role in the improvement of the activated Pt-Pd bimetallic hydrogenation.

From above-mentioned results, it is concluded that Pt-Pd/B₂O₃-Al₂O₃ catalysts have a promising potential for deep aromatic hydrogenation processing for distillate fuel oils and therefore warrant study in more detail.

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Keywords

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