NEW TYPE OF TiN SUPPORT FOR HYDROPROCESSING CATALYST

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TiN supported molybdenum sulfide catalysts showed much higher activity for cleavage of C–C bonds than oxide supported molybdenum sulfide catalysts, indicating the possibility of a new generation of supports for hydroprocessing catalysts.

1. Introduction

Molybdenum sulfide catalysts containing nickel or cobalt promoters have long been used for hydrotreating in the petroleum industry. Oxide supports such as alumina or silica/alumina have been employed in the traditional catalysts. However, improvements in the selectivity of the molybdenum sulfide catalyst for the hydrotreating is required to minimize consumption of hydrogen and to produce clean fuels. The development of new supports that improve the catalytic selectivity appears to be one of the most promising approach for this objective. During the course of study on superior catalysts supports, the authors found that hydrocracking activity of molybdenum sulfide catalysts is highly dependent on the type of supports [1]. The order of effectiveness of the supports is TiO2 > SiO2 > ZrO2 > Al2O3 > MgO. As the next step in the investigation of the catalyst support, many kinds of double oxides such as TiO2·Al2O3 or ZrO2·TiO2 were prepared and tested. Among these candidates some of the double oxides supports gave higher hydrocracking activities than the single oxide supports [2]. However, much higher hydrocracking activity is required for a new generation of hydrotreating catalyst.

In the present work, nitride and carbide supports were prepared and tested with the objective of finding new supports for hydroprocessing catalysts which give higher hydrocracking activities than oxide supports. Titanium was selected as...
the cation species of nitride because of the stability of nitride and the highest hydrocracking activity among the single oxide supports investigated.

2. Experimental

TiN and TiC were synthesized by a thermal plasma arc jet method [3]. Oxide supports were also prepared and used for reference.

The physical properties of these supports are summarized in Table 1. 10 wt% MoO₃, 2 wt% NiO-7 wt% MoO₃ and 10 wt% NiO were loaded on these supports by an impregnation method [5]. The catalysts were subsequently dried under nitrogen atmosphere at 110°C for 16 h then calcined at 300°C for 2 h in a nitrogen atmosphere to prevent oxidation of the supports. The form of these catalysts was powder. The catalysts were presulfided with 5%H₂S-95%H₂ gas for 2 hours before the reaction. The hydrocracking activity of C–C bond and the hydrogenation of the aromatic rings were examined by using model test reactions. The hydrocracking of diphenylmethane (DPM) and the hydrogenation of 1-methylnaphthalene (1-MN) were chosen as probe reactions for estimating hydrocracking and hydrogenation activities, respectively. All the activities of the catalysts were studied under high hydrogen pressure for better understanding of the hydrocracking and hydrogenation activities of the catalysts. A stainless steel microreactor (50 cm³) charged with 0.5 g of the catalyst and 10 cm³ of DPM or 1-MN were used for the hydrocracking or the hydrogenation reaction. The unit was pressurized with H₂ to an initial pressure of 6.9 MPa and then injected into an oven heated at 430°C. The oven was shaken automatically during the reaction. The hydrocracking reaction was performed at 400°C for 60 min, while the hydrogenation reaction of 1-MN was done at 350°C for 60 min. The reactions were repeated at least twice and averaged values were calculated. Reaction products were analyzed by gas chromatography equipped with an OV-1 capillary column (50 m). X-ray photoelectron spectra were obtained using a Shimadzu ASIX-1000 spectrometer with Mg Kα X-ray. For XPS analysis samples were pressed into pellets, which were fixed on the holder. The binding energies, which were referenced to gold (Au 4f₇/₂ = 83.8 eV) evaporated on the sample, were reproducible within +0.1 eV.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Physical properties of supports</th>
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<tbody>
<tr>
<td>Support</td>
<td>S·A (m²/g)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>149</td>
</tr>
<tr>
<td>TiN</td>
<td>53</td>
</tr>
<tr>
<td>TiC</td>
<td>29</td>
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