Hydrodesulfurization Catalyst and Hydrodesulfurization System Compatible with Sulfur-Free Diesel Oil

**Features**

**Application**
The sulfur concentration of diesel oil is restricted to a maximum of 10 to 15 ppm, a sulfur-free level, in Japan, North America, the EU, and other countries. Chiyoda Corporation provides a hydrodesulfurization catalyst (hybrid titania catalyst) that enables production of sulfur-free diesel oil and hydrodesulfurization systems using this catalyst. This catalyst demonstrates a high desulfurization performance for straight-run light gas oil and kerosene, and various oils with a high nitrogen concentration, which are difficult to be desulfurized, such as FCC light cycle oil (LCO), thermal cracked oil, and vacuum gas oil (VGO).

**Background to development of catalyst**
So far, the catalysts used for the commercial hydrodesulfurization of diesel oil have mainly been catalysts of alumina material with such catalyst supports as cobalt, nickel, and molybdenum (alumina catalyst). On the other hand, the potential of titania drew attention as a catalyst support because of its high desulfurization reactivity per unit surface area. However, the conventional titania-based catalyst (titania catalyst) had a significant disadvantage of an exceedingly low surface area and therefore was not used for commercial operations. Chiyoda developed the titania catalyst in the first-step of development, overcome conventional problems using a proprietary catalyst preparation method, and successfully developed a titania catalyst with a higher desulfurization reactivity than a commercially available alumina catalyst. In the second-step of development, we developed a hybrid titania support in pursuit of a revolutionary complex compound of titania and alumina and then developed and commercialized a hybrid titania catalyst and CT-HBT (Chiyoda thoroughly-bred hybrid titania) catalyst.

**Characteristics of CT-HBT catalyst**
The hybrid titania support of the CT-HBT catalyst has a frame that forms nano pores and consists of alumina particles coated with a thin film of titania. Due to this support structure, the CT-HBT catalyst has the features of both the titania catalyst and alumina catalyst shown in Fig. 1. With the CT-HBT catalyst, the characteristics of the titania catalyst are realized at the reaction properties per unit surface area. Furthermore, high activity is achieved since it has a similarly high level of specific surface area as alumina. In addition, this catalyst has a large specific gravity and dramatically reduces the usage volume of expensive titania, enabling the weight to be significantly reduced and costs to be substantially cut compared to when a titania catalyst made with a high purity titania carrier is used.

**Hydrodesulfurization Reactivity of CT-HBT Catalyst**
A comparison of the hydrodesulfurization reactivity of straight diesel oil using the CT-HBT catalyst and commercially available alumina catalyst is shown in Fig. 2. The CT-HBT catalyst has 1.5 times the desulfurization activity of the commercially available alumina catalyst, and the reaction temperature can be lowered by approximately 10°C. Energy savings can be made by operating the unit at a lower reaction temperature, which also enables a longer catalyst life to be achieved.

The transition in reaction temperature in order to maintain the sulfur concentration in purified diesel oil at 10ppm in a hydrogenation and desulfurization test with the CT-HBT catalyst using straight-run light gas oil as the raw material is shown in Fig. 3. The desulfurization activity of this catalyst has been verified to be stable over a long period of time, enabling continuous operation for a period equivalent to two years.
LCO purified with an FCC is put through a desulfurization process to make it sulfur free, enabling conversion into a light diesel oil product that has high added value. The increase in the required reaction temperature in order to maintain the sulfur concentration in the purified oil at 10ppm or less is shown in Fig. 4 for each catalyst during the hydrodesulfurization process for LCO mixed light diesel oil. Due to the fact that desulfurization of the oil becomes more difficult the higher the LCO mixing ratio, the reaction temperature must be increased. However, since processing can be performed at a lower rise in temperature with the CT-HBT catalyst compared with the alumina catalyst, it is more suitable for application in the LCO hydrodesulfurization process.

Support of hydrodesulfurization system
We utilize the merits of being a comprehensive engineering company in order to make proposals that meet the needs of our customers. For example, in addition to supplying catalysts, we can also design, procure and build (or modify) various types of equipment.

Effects or Remarks

Energy saving effect of CT-HBT catalyst
- The hydrodesulfurization system can be operated at a lower reaction temperature than before.
- Compared with the alumina catalyst, the hybrid titania catalyst has a higher hydrodenitrogenation activity at the same hydrodesulfurization activity, which can further reduce the nitrogen concentration in the generated oil.
- The hybrid titania catalyst offers an equivalent hydrodenitrogenation activity at a lower chemical hydrogen consumption than the alumina catalyst.
- The mixed processing of the difficult-to-desulfurize LCO or thermal cracked oil with the straight-run light gas oil will enable conversion to a diesel oil product with high added values.
- If the VGO to be supplied to the FCC is processed using this catalyst to have a low nitrogen concentration, the nitrogen poisoning of the FCC catalyst will be alleviated and the profit improvement of the gasoline distillate can be expected.

Installation in Practice or Schedule

Domestic
- Yamaguchi Refinery, Seibu Oil Co., Ltd.
  Kerosene/Diesel Oil Hydrodesulfurization System (photo) is capable of refining diesel oil containing a maximum 30% LCO
- Other: 2

Overseas
None

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