HYDROGENATION CATALYSTS ON CHARCOAL IN GUARD CHAMBER FOR REMOVING METALS FROM PETROLEUM RESIDUA

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9 Claims

ABSTRACT OF THE DISCLOSURE

Metals and coke precursors are removed from petroleum residua prior to hydrodesulfurization by contacting the residua with a hydrodesulfurization catalyst supported on charcoal or activated carbon so that the metals may be easily recovered by gasifying or burning the carbon base.

BACKGROUND OF THE INVENTION

This invention relates to a method for the removal of metals and coke precursors from heavy feeds to a hydrodesulfurization process.

The hydrodesulfurization of crude petroleum often contain traces of vanadium, nickel and other metals which cause rapid deactivation of sulfur resistant catalysts used in the hydrodesulfurization of such fractions. This is particularly true of residuum fractions as a result of which it has not been practical to refine such fractions by a catalytic hydrodesulfurization process. It has previously been suggested that metals be removed from feeds to a hydrodesulfurization process by first contacting the feedstock with bauxite in the presence or absence of hydrogen under conditions of temperature and pressure such that the metals are deposited on the bauxite as described in U.S. Pat. 2,687,985 filed Jan. 22, 1953, to Porter and Purdy and 2,769,758 filed Mar. 15, 1952, to Porter and Isitt. The use of titania on alumina for the same purpose is described in U.S. Pat. 2,730,487 filed July 1, 1953, to Porter and Purdy.

It is also known to remove asphaltenes as well as metals from a reduced crude prior to desulfurizing the same, by contacting the reduced crude in the presence of hydrogen with a catalyst similar to that used in the subsequent desulfurization stage or with an essentially inert particulate contact material such as tabular alumina, electrician's lead, extruded alumina or a low activity catalyst as described in U.S. Pat. 3,362,901 to Szeppe et al., filed Jan. 11, 1966, and issued Jan. 9, 1968.

While the above processes are successful in removing metals from heavy petroleum fractions, nevertheless it has been found somewhat difficult to remove the metals from the bauxite, alumina or other supports used in the preliminary treating zone.

SUMMARY OF THE INVENTION

In accordance with the present invention the above disadvantages are overcome by first contacting the feedstock in a guard chamber containing a hydrodesulfurization catalyst supported on a charcoal or activated carbon base at elevated temperature and pressure in the presence of hydrogen so that a considerable proportion of the metals and coke precursors are deposited thereon and thereafter passing the thus treated feedstock to a hydrodesulfurization zone under generally more severe conditions than prevails in the first stage whereby the activity of the catalyst is increased and the catalyst life is extended because of reduced metal deposition. In one embodiment the charcoal base can be easily removed by burning or steam gasification to form desirable gas products leaving the metals to be easily recovered. In another embodiment two guard chambers can be used, so that one may be regenerated while the other is on stream. This regeneration may be accomplished either by partial oxidation with air or by gasification with steam. Additional coke will be laid down on the catalyst when on stream by reason of the coke precursors present in the feed.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The charcoal or activated carbon base suitable for use in this invention may be any solid type of carbon capable of supporting metallic catalyst. However it is preferred to use activated carbon which is made by the destructive distillation of carbonaceous material under controlled conditions. The specific area of such a carbon may range from 600 to 2000 square meters per gram.

Any type of sulfide hydrogenation catalyst may be used in conjunction with the charcoal or activated carbon base. Suitable catalysts include one or more of the oxides or sulfides of a metal of Group VIII in combination with metals of Group II-B and VI-B, such as Ni-W, Ni-Mo, Co-Mo, Co-W, Zn-Mo, Zn-W or mixtures thereof. A typical catalyst contains about 0.1 to 20% by weight of a Group VIII metal such as nickel and about 0.1 to 10% by weight of a Group VI-B metal such as tungsten.

The reaction conditions used in the first stage can vary over wide ranges depending on the particular feed. Generally the conditions include pressures of from about 500 to 1500 p.s.i.g., a temperature of about 650 to 950 °F., a feed rate of 0.5 to 20 volumes of feed per volume of catalyst per hour (v/v/hr.) and 1000 to 10,000 s.c.f. per barrel of hydrogen.

The subsequent hydrodesulfurization reaction is accomplished over catalysts which are preferably more active than those used for the preliminary treatment. The active metallic components in the catalyst are a Group VI-B oxide or sulfide, specifically an oxide or sulfide of molybdenum, tungsten, or their mixtures and a Group VIII metal oxide or sulfide, specifically an oxide or sulfide of nickel or cobalt. Suitable catalysts consist of 1 to 15 wt. percent of nickel or cobalt (as oxide), preferably 2 to 10 wt. percent, 5 to 25 wt. percent of tungsten or molybdenum (as oxide), preferably 10 to 20 wt. percent supported on alumina, the alumina preferably containing 1 to 6 wt. percent of silica. A particularly suitable catalyst consists of 3.5 wt. percent of CoO and 12.5 wt. percent MoO3 on alumina containing about 2.0 wt. percent silica and having a maximum surface area in pores having a diameter of 30 to 70 Å as described in application Ser. No. 648,604 filed June 26, 1967, which was issued as U.S. Patent 3,509,044 on April 28, 1970, to Adams and House and the subject matter of which is incorporated herein by reference.

The reaction conditions in the hydrodesulfurization step may range between 500—825 °F., preferably 650—800 °F., 500—2500 p.s.i.g., preferably 800—1800 p.s.i.g., a space velocity of 0.2 to 5.0 v/v/hr., preferably 0.5—2.0, and a hydrogen rate of 500—7500 s.c.f. per barrel, preferably 1000—5000.

The feed stock is preferably a petroleum residuum 30 to 90% of which boils above 900 °F. and which is obtained from crude oils by distillation or treating or by some other type of separation. The residuum may be a blend of high boiling materials such as atmospheric bottoms, vacuum bottoms, deasphalted, and oil distiller bottoms containing about 25 p.p.m. or more each of nickel or vanadium measured as the oxides NiO and V2O5.

The following example is included to illustrate the effectiveness of the instant process for the preliminary
treatment of petroleum residuum prior to hydrodesulfurization thereof without limiting the same.

EXAMPLE

Three runs were carried out using West Texas residuum and Bachaquero residuum as feed. In each case the feed was passed over a nickel-tungsten catalyst (2.3% Ni and 11.4% W) on activated charcoal at a temperature of 800° F., 1000 p.s.i.g., 1 v/v/hr. at a 5000 s.c.f. of H₂ per barrel gas rate. The metals were recovered by burning the charcoal and recovering the metals from the ash.

The following data were obtained:

<table>
<thead>
<tr>
<th>West Texas Feed</th>
<th>Bachaquero Feed</th>
<th>400°F Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run No.</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Prod. Dist.</td>
<td>Feed (%)</td>
<td>Feed (%)</td>
</tr>
<tr>
<td>CO and CO₂</td>
<td>6.8</td>
<td>6.1</td>
</tr>
<tr>
<td>SO₂ and Lower</td>
<td>17.6</td>
<td>11.1</td>
</tr>
<tr>
<td>N₂</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>97.0</td>
</tr>
</tbody>
</table>

Inclusions on Cr₃⁺:

- Gravity, A.P.I.: 18.3 20.0 25.5 15.2 24.7
- Sulfur, wt. percent: 2.2 0.6 6.6 2.4 0.53
- Cond. carbon, wt. percent: 6.8 6.8 2.5 10.6 3.4
- V, p.p.m.: 24 <1 1 400 36
- Ni, p.p.m.: 12 <1 1 87 12

1 Wt. percent on feed (output basis).

The above data show that metal removal from the pretreatment was excellent (<1 p.p.m.) with West Texas residuum and satisfactory with the high-metal-content Bachaquero residuum (<70 p.p.m.). The Conradson carbon level of both feed stocks was reduced considerably, indicating the removal of coke precursors. Furthermore more than 60% desulfurization was realized. Substantially complete desulfurization can thus be obtained in a second-stage conventional hydrodesulfurization step using cobalt molybdate catalyst with high catalyst activity maintenance level for a long period of time due to the previous removal of metals from the feed.

The nature of the present invention having thus been fully set forth and specific examples of the same given, what is claimed as new, useful, and unobvious and desired to be secured by Letters Patent is:

1. A process for the removal of metals and coke precursors from a hydrocarbon residuum containing the same which comprises contacting said residuum at 650–950° F., 500–1500 p.s.i.g., a feed rate of 0.5 to 20 volumes of residuum per volume of catalyst per hour and in the presence of 1000 to 10,000 standard cubic feet of hydrogen per barrel of feed and a catalyst comprising an oxide or sulfide of a metal of Group II–B or VI–B together with a Group VIII metal on charcoal for a period of time to remove a substantial quantity of the metals.

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U.S. Cl. X.R.

208—216, 253; 252—447