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HYDROPROCESSING OF RESIDS WITH METAL ADSORPTION ON THE SECOND STAGE CATALYST**Fritz A. Smith, Haddonfield, N.J., and Lothar H. Riekert, Ludwigshafen, Germany, assignors to Mobil Oil Corporation, New York, N.Y.****No Drawing. Filed Oct. 12, 1971, Ser. No. 188,601****Int. Cl. C10g 23/02****U.S. Cl. 208—212****2 Claims****ABSTRACT OF THE DISCLOSURE**

This invention provides a method for the hydroprocessing of a hydrocarbon charge stock over a catalyst characterized by a strong hydrogenation activity at low temperatures followed by conversion of the resulting product at high temperatures in the presence of a catalyst of low hydrogenation activity. The first stage reaction is conducted at a temperature in the range of 600–785° F. and exceeds 800° F.

BACKGROUND OF THE INVENTION**Field of the invention**

This case deals with the hydroprocessing of resids in two distinct reaction stages. More specifically, the first stage is characterized by temperatures between 600 and 785° F. and a sulfur resistant catalyst. The second stage is characterized by temperatures exceeding 800° F. and a catalyst whose hydrogenation activity is less than the catalyst of the first stage.

Description of the prior art

Various different metallic elements have been found in crude oils. Many of these metals are found only in trace amounts of less than 1 part per billion. However, metals such as calcium, vanadium, iron, nickel, and copper do occur in large concentrations, up to 0.1%. These metal contaminants have an adverse effect on all catalytic processing operations because of their tendency to accumulate on the catalyst, change the catalyst composition and thereby deactivate the catalyst or change its catalytic activity.

Crude petroleum oils, toppedcrudes or other hydrocarbon fractions and/or distillates obtained therefrom, depending upon the source of the crude, contain varying amounts of non-metallic and metallic impurities. The metals may occur in several different forms. Metal oxides or metal sulfides are easily removed by methods such as filtration and water washing. However, the metal contaminants also occur as relatively thermally stable metallo-organic complexes such as metal porphyrins and derivatives thereof along with complexes which are not completely identifiable. It has been found that most of the metallo-organic complexes are associated with the asphaltenes and become concentrated in the residual fractions. Some metallo-organic complexes are volatile enough and will be carried over in distillate fractions rather than remain with the bottom product. The asphaltenes are generally considered to be non-distillable, of high molecular weight, and contain nitrogen, sulfur, oxygen and metal contaminants which when subjected to heat will coagulate and/or polymerize and become difficult to handle in further treatment.

The distillation bottoms are either sold as fuels or charged to a coking unit, where the metals end up in the petroleum coke. This petroleum coke is often sold as relatively cheap fuel. However, since these fuels also contain considerable amounts of sulfur, up to 6 percent, they may no longer be acceptable in the future, because of air pollution restrictions, unless the sulfur content is

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reduced. Unfortunately, the catalytic desulfurization of hydrocarbon stocks is adversely affected by the metals content. Catalysts employed for the hydrodesulfurization of oils tend to become deactivated and fouled by hydrocarbonaceous deposits along with other impurities encountered in the charge stock. The extent and rapidity of fouling depends in large part upon the source and boiling range of the charge being treated. Therefore, a process to remove the metals from hydrocarbon stocks is highly desirable and technically important.

It may be noted that there are several U.S. patents that describe two-stage hydrogenation processes for the removal of sulfur and metals from petroleum materials. Among these are U.S. 3,362,901 issued to Szepe, U.S. 3,180,820 issued to Gleim and U.S. 3,472,759 issued to Masologites. None of these patents describes the specific range of temperatures, the particular catalyst and the order of treatment that is embodied in the present invention. Thus, the uniqueness of the present process renders in the particular set of temperatures and catalysts that are used to treat the hydrocarbon stock.

SUMMARY OF THE INVENTION

Hydrocarbon resids are hydroprocessed over catalysts characterized by a strong hydrogenation activity at low temperatures followed by conversion of the resulting product at high temperatures in the presence of a catalyst of low hydrogenation activity. The first stage reaction is conducted at a temperature in the range of 600–785° F. with a catalyst that has a hydrogenation activity in excess of 15. The second stage reaction is conducted at a temperature exceeding 800° F. with a catalyst having a hydrogenation activity below about 30. The hydrogen activity of the catalyst in the first stage should be at least 5 units greater than the activity of the catalyst in the second stage. Representative catalysts used in the first stage include cobalt-molybdenum on alumina and nickel-molybdenum on alumina. Typical catalysts for use in the second stage include zinc oxide on alumina and ferric oxide on alumina and tin or coke. The first stage hydrogenation should be conducted at pressures in the range of 1,500 to 3,000 p.s.i.g. The second stage hydrogenation should be conducted at 500 to 2,000 p.s.i.g. It should be also understood that this invention contemplates the reaction in the first stage must be conducted in the presence of hydrogen. For example, a hydrogen recycle ratio of 500 to 10,000 s.c.f./b. of charge stock should be used.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The present invention is directed to a method in combination of steps for effectively reducing the non-metallic and metallic impurities encountered in hydrocarbon charge stocks. More particularly, the present invention is based on the finding that the removal of metallic and non-metallic impurities is enhanced under hydrogenating conditions and best effected in a separate contacting step in the presence of particularly selected catalysts for each step and at operating conditions most suitable for effecting removal of nitrogen and sulfur compounds in an initial step as distinguished from those conditions most effective for removing metal containing compounds in the hydrocarbon charge in the second stage.

Thus, the invention is predicated on the discovery that the removal of metals, sulfur and nitrogen contaminants is most efficiently carried out at different levels of hydrogenation activity within particularly selected temperature and pressure conditions. Sulfur and nitrogen contaminants are primarily removed from the charge in the first stage and metals are primarily removed in the second stage. The first stage is characterized by the introduction of a considerable quantity of hydrogen.

Hydrogenation activity of a catalyst is herein defined by the method described by Meyers et al., Journal of Chemical and Engineering Data, volume 7, page 258, 1962. It is designated as the weight percent conversion of benzene to hydrogenated products over the catalyst at 1,050 p.s.i.g., a space velocity of 2 volumes/hour/volume, 700° F. and 4,000 s.c.f. of hydrogen charge/bbl. hydrocarbon charge.

The first stage catalyst in the method of the present invention is broadly characterized as a hydrogenation catalyst which is tolerant of sulfur and nitrogen and which can be employed in an operating cycle or on-stream life that is economically attractive. The catalyst should have a hydrogenation activity greater than about 15. Representative catalysts used for this purpose include cobalt molybdate on alumina with or without small amounts of silica, nickel molybdate on alumina with or without small amounts of silica, nickel sulfide, tungsten sulfide, nickel-tungsten sulfide alone or on a support material such as alumina which may or may not contain small amounts of combined silica. Other suitable and known desulfurization catalysts may also be employed.

The second stage catalyst is preferably a solid porous material which can adsorb relatively large amounts of released metal contaminants at the mild hydrogenating conditions required of it. It should be a low density material of relatively high porosity and have at least some pores significantly larger than the molecule of the metallo-organo complexes or compounds encountered in the hydrocarbon charge material during the demetallizing step. Suitable solid materials which may be used for this purpose include spent silica-alumina cracking catalyst, petroleum coke, large pore alumina and clays. The hydrogenation activity of this catalyst is supplied by one or more hydrogenation components dispersed throughout the large pore, low density particulate material. The hydrogenation metal component of the demetallizing catalyst is selected from the class of metals comprising cobalt, nickel, copper, tin, molybdenum, tungsten and iron. The catalyst should have a hydrogenation activity below about 30. The demetallizing catalyst eventually becomes contaminated by metal deposits of nickel, vanadium, iron and copper and thus will eventually be discarded from the process when the metals level exceeds an undesirable limit for economically effecting further metals removal.

In the method of the present invention, the first zone reaction is of relatively strong hydrogenation activity and sufficiently severe to remove predominantly sulfur and nitrogen contaminants. The second zone reaction is one of relatively mild hydrogenation, but sufficiently severe to remove or detach metals found in the metallo-organic complexes for deposit of the metals upon the porous solid contact material used therein.

Thus, the process of the present invention is directed to a particular sequence of hydroprocessing steps in separate contact zones wherein the hydrocarbon charge is initially contacted in the presence of hydrogen and under desulfurization and denitrogenation conditions in the presence of a sulfur and nitrogen tolerant catalyst. Thereafter, the hydrocarbon charge is contacted with a finely divided solid particulate material having hydrogenation activity distributed in a support material having an average pore size of at least 80 Å. and preferably about 150 to 300 Å.

In a particularly preferred embodiment, a relatively small amount of hydrogenation activity in the range of from about 0.2 to about 15 will be provided by the solid contact material by combining one or more hydrogenating components with the low density, high porosity support. The porous support may be one having little or no acid activity such as provided by spent silica-alumina cracking catalysts.

The operating conditions of temperature, pressure and space velocity employed in the separate zones are inter-

related as a function of the catalyst's initial hydrogenation activity and are thus selected in order to optimize desulfurization and denitrogenation in the first zone and demetallization in the second zone. It is preferred to employ pressures in the range of 1,500 to 3,000 p.s.i.g. in the first stage and pressures of 500 to 2,000 p.s.i.g. in the second stage. In a preferred embodiment, the first stage temperature is in the range of 600–785° F. and the second stage reaction is conducted at a temperature that exceeds 800° F. The hydrogen activity of the catalyst in the first stage should be at least 5 units greater than the activity of the catalyst in the second stage. The space velocity conditions employed in each contact zone will be selected from within the range of about 0.3 to about 4.0 LHSV and generally will be about the same in each zone.

While not wishing to be limited by any specific theory, it is believed that by limiting the first stage temperature to a maximum of 785° F., the amount of asphaltene that agglomerates or polymerizes and therefore is deposited on the catalyst is greatly reduced. Thus, the first stage catalyst will function effectively for longer periods of time when the temperature is limited in the above manner. This limitation also permits the second stage treatment to be carried out at higher temperatures and conducted over a cheap disposable catalyst.

The present invention is capable of treating many different hydrocarbon fractions that vary in boiling range. These include for example, full boiling range crudes, topped crude oils and distillates therefrom, atmospheric distillates, cycle oils, light and heavy vacuum gas oils and coker gas oils.

The following examples will illustrate the utility of this present invention.

EXAMPLE 1

A West Texas sour resid was contacted with a 100% nickel tungsten sulfide catalyst, having a hydrogen activity of about 40, at 600° F., 1,500 p.s.i.g. and 1.5 LHSV. The resid was then contacted with a cobalt-molybdenum alumina catalyst whose hydrogen activity was 25.7. Table I indicates that this two-step treatment enhances the removal of sulfur, metals and nitrogen as compared to treating the raw resid with only the cobalt-molybdenum alumina catalyst.

TABLE I

Stock	Mildly pretreated over NiWS then contacted with CoMo/Al ₂ O ₃	Raw resid contacted with only CoMo/Al ₂ O ₃
Operating conditions:		
Temperature.....	750	800
Pressure.....	2,000	2,000
LHSV, volume of oil/hour/volume of catalyst.....	0.93	0.92
Percent:		
Desulfurization.....	79.4	88.6
Demetallation.....	89.3	95.5
Denitrogenation....	19.4	25.0

EXAMPLE 2

Kuwait short resid was hydroprocessed over CoMoO₄ on Al₂O₃ at temperatures that increased through the catalyst bed from 600 to 720° F. at a pressure of 2,000 p.s.i.g. The CoMoO₄ on Al₂O₃ catalyst consisted of 3 percent CoO and 12 percent MoO₄ and had a hydrogen activity of about 20. The treated stock was then passed over a tin impregnated coke catalyst at 800 to 808° F. The tin impregnated coke catalyst had a hydrogen activity of less than about 1. The effectiveness of this process is shown in Table II.

TABLE II

Catalyst: CoMoO₄ on Al₂O₃ in front of 1% Sn on petroleum coke

Conditions:							
Hours on resid.	4	6	10	22	50	70	
Max. temp. (° F.) of tin on coke catalyst	800	805	805	805	808	806	
LHSV (overall)	0.44	0.44	0.44	0.44	0.38	0.27	
Charge stock							
Analysis:							
Conradson carbon residue, percent	16.5			15.0	15.1	14.4	
Hydrogen, percent	10.3			10.79	10.71	10.81	
Sulfur, percent	5.3	0.42	1.8	3.5	3.3	3.1	3.0
Ni, p.p.m.	29	1.5	10	21	21	23	19
V, p.p.m.	95	5.9	28	61	61	65	54

What is claimed is:

1. A method for the hydroprocessing of a hydrocarbon charge stock in order to lower the sulfur, nitrogen and metal content thereof which comprises contacting said hydrocarbon charge in a first stage with a catalyst comprising nickel-tungsten sulfide at a temperature in the range of about 600 to about 785° F., and at a pressure in the range of about 1,500 to about 3,000 p.s.i.g. in the presence of hydrogen, and contacting the resultant product in a second stage with a catalyst comprising cobalt-molybdenum on alumina having an average pore size of at least 80 Angstroms wherein metal compounds present in said charge stock are adsorbed at a temperature in

excess of 800° F., and at a pressure in the range of about 500 to about 2,000 p.s.i.g.

2. A method for the hydroprocessing of a hydrocarbon charge stock in order to lower the sulfur, nitrogen and metal content thereof which comprises contacting said hydrocarbon charge in a first stage with a catalyst comprising CoMoO₄, at a temperature in the range of about 600 to about 785° F., and at a pressure in the range of about 1,500 to about 3,000 p.s.i.g. in the presence of hydrogen, and contacting the resultant product in a second stage with a catalyst comprising tin impregnated on coke at a temperature in excess of 800° F., and at a pressure in the range of about 500 to about 2,000 p.s.i.g.

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