HYDROISOMERIZATION WITH REDUCED HYDROCRACKING

FIELD OF THE INVENTION

This invention relates to the hydroisomerization of feeds containing heteroatoms, e.g., sulfur or oxygen. More particularly, this invention relates to the hydroisomerization of feeds over a catalyst containing a Group VIII non-noble metal and a hydrocracking suppressant.

BACKGROUND OF THE INVENTION

Isomerization processes generally require the removal, e.g., by hydrotreating, of sulfur and nitrogen compounds that can rapidly deactivate or poison the relatively expensive isomerization process catalyst. Consequently, feeds to be isomerized are first contacted with a sulfur tolerant catalyst in the presence of hydrogen for minimizing the amount of sulfur in the feed.

Additionally, isomerization processes, particularly those carried out in the presence of hydrogen, are effected with unsulfided catalysts. As a consequence, hydrogenolysis, e.g., hydrocracking, occurs early in the processing and produces significant amounts of gaseous products, e.g., methane or C_1-C_4 hydrocarbons. A process, therefore, that can eliminate or substantially reduce the hydrogenolysis aspect of the process can be more efficient and more economic because of increased yields of desired products and decreased yields of gaseous products.

SUMMARY OF THE INVENTION

In accordance with this invention a hydroisomerization process is conducted in the presence of hydrogen and a catalyst comprising a Group VIII non-noble metal and a hydrocracking suppressant. The hydrocracking suppressant may be either a Group 1B metal or a source of sulfur, usually in the form of a sulfided catalytically active metal, or a Group 1B metal and a source of sulfur. Hydrocracking suppression can be effectively measured by suppressing methane, since hydrocracking most easily occurs through terminal cracking. The

process is conducted with hydrocarbon containing feeds at usual hydroisomerization conditions. Generally, the process of this invention will lead to methane yields of less than about 5 wt% based on total 700°F+ conversion, preferably less than about 2 wt%, more preferably less than about 1 wt%, and still more preferably less than about 0.5 wt%. In a preferred embodiment, the catalyst also contains effective amounts of a Group VI metal.

Typical hydroisomerization conditions are well known in the literature and can vary widely. For example, broad and preferred ranges for these conditions are shown in the following table:

CONDITION	BROAD	PREFERRED
Temperature, °F	300-900(149-482°C)	550-750(288-399°C)
Total pressure, psig	0-2500	300-1200
Hydrogen Treat Rate, SCF/B	500-5000	2000-4000
Hydrogen Consumption Rate, SCF/B	50-500	100-300

The catalysts useful in this invention preferably contain an acid function as well as the hydrocracking suppressant. The hydrocracking suppressant may be either a Group 1B metal, e.g., preferably copper, in amounts of about 0.1-10wt%, or a source of sulfur, or both. The source of sulfur can be provided by pre-sulfiding the catalyst by known methods, for example, by treatment with hydrogen sulfide until breakthrough occurs. The use of pre-sulfided non-noble metal catalysts for hydroisomerization is believed to be unprecedented.

When feeds that are essentially free of sulfur are processed in accordance with this invention, sulfur may be stripped from a sulfided catalyst. As a consequence, it will be preferred to add small amounts of sulfur with the feed, either continuously or periodically to maintain a desired level of sulfur in the catalyst. Catalysts containing sulfur typically have at least about 0.01 wt% sulfur, preferably about 0.01 to 20% sulfur, preferably 0.1 to 10 wt%.

The Group VIII non-noble metals may include nickel, cobalt, tungsten, preferably nickel or cobalt, more preferably cobalt. The Group VIII metal is usually present in catalytically effective amounts, that is, ranging from 0.5 to 20 wt%. Preferably, a Group VI metal is incorporated into the catalyst, e.g., molybdenum, in amounts of about 1-20 wt%.

The acid functionality can be furnished by a support with which the catalytic metal or metals can be composited in well known methods. The support can be any refractory oxide or mixture of refractory oxides or zeolites or mixtures thereof. Preferred supports include silica, alumina, silica-alumina, silica-alumina-phosphates, titania, zirconia, vanadia and other Group III, IV, V or VI oxides, as well as Y sieves, such as ultra stable Y sieves. Preferred supports include alumina and silica-alumina, more preferably silica-alumina where the silica concentration of the bulk support is less than about 50 wt%, preferably less than about 35 wt%, more preferably 15-30 wt%. When alumina is used as the support, small amounts of chlorine or fluorine may be incorporated into the support to provide the acid functionality.

A preferred supported catalyst has surface areas in the range of about 180-400 m^2/gm, preferably 230-350 m^2/gm, and a pore volume of 0.3 to 1.0 ml/gm, preferably 0.35 to 0.75 ml/gm, a bulk density of about 0.5-1.0 g/ml, and a side crushing strength of about 0.8 to 3.5 kg/mm.

The preparation of preferred amorphous silica-alumina microspheres for use as supports is described in Ryland, Lloyd B., Tamele, M.W., and Wilson, J.N., Cracking Catalysts, Catalysis; Volume VII, Ed. Paul H. Emmett, Reinhold Publishing Corporation, New York, 1960.

During hydroisomerization, the 700°F+ conversion to 700°F- ranges from about 20-80%, preferably 30-70%, more preferably about 40-60%; and essentially all olefins and oxygenated products are hydrogenated.

The feed can be any hydrocarbon containing material having a final boiling point of less than about 1050°F, (566°C). A particularly preferred feed is a C_5+ material derived from a non-shifting Fischer-Tropsch process.

The feed materials that are hydroisomerized are typically waxy feeds, C5+, preferably boiling above about 350°F (177°C), more preferably above about 550°F (288°C), and are preferably obtained from a Fischer-Tropsch process which produces substantially normal paraffins, or may be obtained from slack waxes. Slack waxes are the by-products of dewaxing operations where a diluent such as propane or a ketone (e.g., methylethyl ketone, methylisobutyl ketone) or other diluent is employed to promote wax crystal growth, the wax being removed from the lubricating oil by filtration or other suitable means. The slack waxes are generally paraffinic in nature, boil above about 600°F (315°C), preferably in the range of 600°F to 1050°F (315-566°C) and may contain from about 1 to about 35 wt% oil. Waxes with lower oil contents, e.g., 5-20 wt% are preferred; however, waxy distillates or raffinates containing 5-45% wax may also be used as feeds. Slack waxes are usually freed of polynuclear aromatics and hetero-atom compounds by techniques known in the art; e.g., mild hydrotreating as described in U.S. Patent 4,900,707, which also reduces sulfur and nitrogen levels. Feeds which contain high levels of sulfur, e.g., >30 ppm sulfur, may also be used as the catalyst described here is sulfur tolerant. In addition, feeds such as gas field condensates may be used as feeds or other petroleum derived feeds with high sulfur levels that require hydroisomerization to improve its properties. A distillation showing the fractional make up (±10 wt% for each fraction) for a typical Fischer-Tropsch process feed stock follows:

Boiling Temperature Ranges	Wt% of Fraction
IBP-320°F (160°C)	13
320-500°F (160-260°C)	23
500-700°F (260-371°C)	19
700-1050°F (371-566°C)	34
1050°F+ (566°C+)	11
Total	100

The feed may be treated or untreated as regarding the removal of hetero-atoms containing compounds, e.g., sulfur and oxygen containing compounds. (Nitrogen does not seem to be a problem, either its presence or absence.) However, when the feed is treated, essentially all of the sulfur and oxygen should be removed, that is, to sulfur levels of less than about 10 wppm,

and oxygen levels of less than about 10 wppm. Such feeds are characterized by the substantial absence of sulfur and oxygen. Hydrotreating is effected by any of the well known hydrotreating, e.g., hydrodesulfurization, processes known in the literature.

The catalyst can be prepared by any well known method, e.g., impregnation with an aqueous salt, incipient wetness technique, followed by drying at about 125-150°C for 1-24 hours, calcination at about 300-500°C for about 1-6 hours, reduction by treatment with a hydrogen or a hydrogen containing gas, and, if desired, sulfiding by treatment with a sulfur containing gas, e.g., H_2S at elevated temperatures. The catalyst will then have about 0.01 to 10 wt% sulfur. The metals can be composited or added to the catalyst either serially, in any order, or by co-impregnation of two or more metals.

The following examples will serve to illustrate, but not limit this invention.

Example 1

A commercial Co-Mo catalyst on a SiO_2-Al_2O_3 support containing 20-30 wt% bulk silica was reduced at 370°C for 3 hours in hydrogen. The catalyst was used to hydroisomerize n-heptane as a model compound representing the more refractory paraffins present in condensate. The results of the isomerization test are found in the following table.

Example 2

The Co-Mo catalyst of Example 1 was impregnated with an aqueous solution of copper nitrate to introduce 0.3 wt% Cu. The catalyst was calcined in air at 370°C and reduced in hydrogen at 370°C for 3 hours. The Co–Mo–Cu catalyst was used to hydroisomerize n-heptane. The results are presented in the table below.

Example 3

The Co-Mo catalyst of Example 1 was reduced in hydrogen at

370°C for 3 hours and breakthrough sulfided with dilute H_2S in H_2 at 370°C. The catalyst was H_2 stripped at the same temperature for 2 hours to remove any chemisorbed H_2S. The Co-Mo-S catalyst was used to hydroisomerize n–heptane. The results are included in the following table.

The catalyst of Example 1, while active for hydroisomerization, has extremely high hydrocracking activity as evidenced by very high methane and n-butane yields and the destruction of normal and isoheptanes. Liquid yield is decreased to a value < 70 wt%.

The catalysts of this invention, Co-Mo-Cu and Co-Mo-S, the catalysts of Examples 2 and 3, are preferred hydroisomerization catalysts on the basis of higher selectivity to isomerized product and substantially decreased hyrocracking activity. In both cases the yields of liquid product exceed 92 wt%, and the formation of isoheptanes is roughly 40% greater than that of Example 1. While not shown in the table, the combination of sulfur with Cu would offer additional yield and selectivity credits relative to those of Examples 2 and 3.

ISOMERIZATION OF HEPTANE WITH
SULFIDED CO-MO AND CO-MO-CU CATALYSTS

n-Heptane, 425°C, 100 psig, 5 W/H/W, H_2/Oil=6

EXAMPLE	1	2	3
Catalyst	Co-Mo	Co-Mo-Cu	Co-Mo-S
C_1	6.4	1.4	0.2
i-C_4	0.5	0.3	0.1
n-C_4	4.0	0.8	1.0
n-C_7	56.3	77.5	77.7
2,4-DMP	0.4	0.6	0.4
2-Me-Hex	4.6	6.2	6.5
3-Me-Hex	6.4	8.6	9.6
i-C_7's	11.4	15.4	16.6

CLAIMS:

1. A hydroisomerization process comprising: contacting a 350°F+ hydrocarbon containing feed in the presence of hydrogen and a catalyst having an acidic functionality and comprising a Group VIII non-noble metal and a hydrocracking suppressant.

2. The process of claim 1 wherein the suppressant is selected from the group consisting of a Group 1B metal, sulfur or mixtures thereof.

3. The process of claim 1 wherein the suppressant is a Group 1B metal.

4. The process of claim 1 wherein the suppressant is in the form of a pre-sulfided catalyst.

5. The process of claim 1 wherein the catalyst also contains a Group VI metal.

6. The process of claim 1 wherein the catalyst comprises cobalt and molybdenum in catalytically effective amounts.

7. The process of claim 6 wherein the acidic component is in the form of a silica-alumina support.

8. The process of claim 7 wherein the silica content is less than about 50 wt%.

9. The process of claim 8 wherein the silica content is about 15-30wt%.

10. The process of claim 4 wherein sulfur is present on the catalyst in an amount of about 0.1-10 wt%.