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CONVERSION OF HYDROCARBONS

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This invention relates particularly to the conversion of hydrocarbons in the presence of a specially prepared catalyst.

In a broad aspect the present invention relates to a hydrocarbon conversion process which comprises subjecting said hydrocarbon to conversion in the presence of a catalyst comprising a mechanical mixture of a suitable supporting material and sublimed molybdenum oxide.

In one specific embodiment, the present invention relates to a hydrocarbon conversion process which comprises subjecting said hydrocarbon to conversion at a temperature within the range of about 600° to about 1200° F. in the presence of a catalyst comprising a mechanical mixture of alumina and sublimed molybdenic oxide.

The broad scope of the present invention contemplates the conversion of hydrocarbons in the presence of a specially prepared catalyst, and the particular catalytic reactions to be effected in any given operation will depend upon the charging stock to the process and the conditions of operation employed. The present invention is particularly applicable to the type of process known as hydroforming. In this process gasoline or naphtha of relatively low anti-knock characteristics is subjected to treatment in the presence of the catalyst at a temperature within the range of about 900 to about 1100° F. and a superatmospheric pressure of about 50 to about 2000 pounds per square inch or more. In the hydroforming process, hydrogen, either from an external source or recovered from within the process, is supplied to the reaction zone, but there is no net consumption of hydrogen and in fact the quantity of hydrogen produced exceeds the quantity thereof consumed in the process. In this process aromatic hydrocarbons are produced to a considerable extent. The invention also is applicable to the reforming of gasoline or naphtha under substantially the same conditions but in the absence of added or recycled hydrogen.

Another process contemplated by the present invention is hydrocracking, in which operation an oil boiling above the range of gasoline is subjected to contact with the catalyst in the presence of hydrogen at a temperature within the range of about 800 to about 1000° F. and pressures ranging from atmospheric to 1000 pounds per square inch or more. In this process, there usually is a net consumption of hydrogen, and the primary desired product is gasoline of high anti-knock characteristics.

An example of another process contemplated by the present invention is the refining of oil and particularly gasoline to remove undesirable impurities and particularly sulphur. Desulphurization of gasoline may be effected in the pres-

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ence of the catalyst at a temperature within the range of from about 600 to about 700 and, in some cases, as high as 750° F., at atmospheric or slightly superatmospheric pressures which generally are not in excess of about 50 pounds. It is also within the scope of the invention to effect the refining treatment in the presence of hydrogen.

The hereinbefore recited processes are examples in which the charging stocks to the process comprise a mixture of hydrocarbons. The present invention is also applicable to the treatment of a more selected charging stock to effect dehydrogenation and/or dehydrocyclization reactions. For example, pentane may be subjected to treatment in the presence of the catalyst to effect dehydrogenation thereof into amylene. Similarly, hexane may be subjected to conversion in the presence of the catalyst to form hexylene and/or benzene. Likewise, heptanes, octanes, nonanes, etc., may be similarly subjected to treatment to form the corresponding olefin and/or aromatic hydrocarbon. In addition, mono-olefinic hydrocarbons may be subjected to treatment in the presence of the catalyst to form the corresponding di-olefinic hydrocarbons. The dehydrogenation and/or dehydrocyclization reactions may be effected within the broad temperature range of about 800 to about 1200° F., and under low pressures which may be subatmospheric, atmospheric or moderately superatmospheric, generally not in excess of about 50 pounds per square inch. The particular temperature to be employed in any given operation will depend upon the specific charging stock to the process and the products desired.

It is understood that, when selecting the particular temperature and pressure to be employed in any given operation, the time of contact must also be considered, as well as the activity of the particular catalyst being used. The activity of the catalyst will depend somewhat on the specific method of manufacture as will be hereinafter set forth. In addition, it is understood that the reactions hereinbefore set forth are typical of those comprised within the scope of the present invention and that many, if not all, of these reactions may occur to some extent in any particular operation of the process.

As hereinbefore set forth, the primary feature of the present invention is the use in the conversion of hydrocarbons of a specially prepared catalyst comprising a mechanical mixture of a suitable supporting material and sublimed molybdenum oxide. In the ordinary manufacture of catalysts containing molybdenum oxide, it is the practice to prepare such catalysts from commercially available molybdic oxide (MoO_3). Since this oxide as produced commercially is a coarse, dense material, it is the customary prac-

tice, when forming composite catalyst, to use the molybdc oxide in the form of a solution or to convert it into another molybdenum compound and then use the molybdenum compound so prepared in compositing with the supporting material. It is apparent to those skilled in the art that the manufacture of composite catalysts in this way is an involved and expensive procedure. I have found that hydrocarbons may be converted in the presence of a molybdenum oxide-containing catalysts prepared in a simple and inexpensive method from sublimed molybdc oxide. The sublimed molybdc oxide is a very light, fluffy powder that is extremely active. Because of the fine particles, the molybdc oxide may be evenly distributed upon the support merely by mixing the dry powders and pelleting. To illustrate the difference in the sublimed molybdc oxide and the ordinary molybdc oxide, the former has an apparent bulk density of 0.138 gram per cc., as compared to an apparent bulk density of 0.795 gram per cc. for the ordinary molybdc oxide.

In accordance with the invention the sublimed molybdc oxide is composited by mechanical mixing with a supporting material. Any suitable porous supporting material may be used, including aluminum oxide, magnesium oxide, activated bentonite clays, activated montmorillonite clays, kieselguhr, etc. In preparing the supporting materials, some precautions are necessary to insure that they possess the proper physical and chemical characteristics. For example, when using alumina, which is the preferred supporting material of the present invention, it is essential that it be of the gamma-alumina form and not of the inactive alpha form. The aluminum oxide may be obtained from natural oxide minerals, such as bauxite, or from carbonates, such as dawsonite, or it may be prepared by precipitation of aluminum oxide from solutions of aluminum salts such as aluminum sulphate, aluminum chloride, etc., and the precipitate subsequently dehydrated by heat.

As hereinbefore set forth, one of the primary advantages of the present invention is that the catalyst may readily and cheaply be prepared by mechanically mixing of a commercially available aluminum oxide, such as grade A Activated Alumina, in a dry powdered condition with sublimed molybdenum oxide. These mixed powders may then be used as the catalyst or preferably a suitable lubricant is added and the mixture is then pelleted or otherwise formed into granules.

Any suitable lubricant may be used to facilitate pelleting of the powder and may comprise, for example, rosin, graphite, hydrogenated coconut oil, stearic acid, starch, etc.

However, it is also within the scope of the invention to manufacture the composite catalyst by first preparing an alumina gel or hydrous precipitate by reacting a soluble aluminum salt with ammonium hydroxide or ammonium carbonate, or by reacting aluminum metal with a weak dilute acid to form an aluminum sol, which is coagulated by heat or a small amount of base, or by forming such a gel by other methods. The alumina gel in a wet or undried state is then intimately mixed with the molybdc oxide, the mixture dried and subsequently formed into desired shapes by pelleting or otherwise.

In general, the molybdc oxide will comprise from about 2 to about 40% of the composite catalyst. The activity of the particular catalyst will depend on the amount of molybdc oxide and on

its specific method of manufacture. The best catalysts are obtained when molybdc oxide is uniformly distributed throughout the support and it is therefore preferred that the mechanical mixing be efficient. As hereinbefore set forth, the powdered sublimed molybdc oxide is in a very fine state of subdivision and lends itself to ready uniform distribution throughout the composite catalyst mass.

The operation of the process is relatively simple and may take any of the conventional forms. Fixed bed processes are of the type in which the catalyst is disposed within tubes or chambers maintained under the desired temperature and pressure conditions, and the hydrocarbons passed over the catalyst. Fluidized operations comprise passing the hydrocarbon vapors in admixture with the catalyst powders through a reaction zone with a velocity regulated to obtain hindered settling in the reaction zone. In this type of operation the hydrocarbons pass through the reaction zone at a greater velocity than does the catalyst, the operation being controlled so that the catalyst may be removed from the lower portion of the reaction zone while the hydrocarbons are removed from the upper portion thereof. Another suitable type of operation is the moving bed process in which the catalyst is passed countercurrently to the hydrocarbons. Still another type of operation is the suspensoid process in which the catalyst and hydrocarbons are admixed to form a slurry and the slurry is passed into the reaction zone.

It is understood that the present invention is not limited to any particular process flow and that any suitable system for effecting the desired conversion may be employed.

The following example further illustrates the novelty and utility of the present invention.

Example

The catalyst was prepared by mixing 20 grams of sublimed molybdenum oxide, having an apparent bulk density of 0.138 gram per cc., and 20 grams of powdered grade A Activated Alumina in a pebble mill. After mixing for an hour, 4% of rosin was added as a lubricant and the mixture was pelleted. The rosin was removed by heating in air at 932° F.

Naphtha having an Engler initial boiling point of 217° F., an end boiling point of 283° F., a bromine number of 0.3, a toluene content of 8.5% by volume, and an A. S. T. M. octane number of 58 was subjected to hydroforming in the presence of the above catalyst and 3.5 moles of hydrogen per mole of naphtha at a temperature of 960° F., a pressure of 1000 pounds per square inch and a weight hourly space velocity of one. The space velocity is defined as the weight of naphtha per hour per weight of catalyst in the reaction zone. The products obtained are as follows:

Recoveries in weight per cent of charge:

Liquid	83.2
Gas other than hydrogen	6.6
Hydrogen formed	2.4
Carbon	0.2
Total	92.4

The analysis of the liquid product boiling between 194 and 248° F. is as follows:

Refractive index at 20° C.	1.4473
Bromine number	5
Wt. per cent of toluene	51.5

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The volume per cent of toluene based on the charge amounted to 16%, which is 18% by weight.

It will be observed that the carbon formation is extremely low and amounted to only 0.2% by weight of the charge. This low carbon formation and the relatively high toluene yield, as well as the simple and cheap method of manufacturing the catalyst, exemplify the advantages of the present process.

I claim as my invention:

1. A hydrocarbon conversion process which comprises subjecting said hydrocarbon to conversion in the presence of a catalyst comprising a mechanical mixture of a porous supporting material and sublimed molybdenum oxide.

2. A hydrocarbon conversion process which comprises subjecting said hydrocarbon to conversion in the presence of a catalyst comprising a mechanical mixture of gamma alumina and sublimed molybdic oxide.

3. A hydrocarbon conversion process which comprises subjecting said hydrocarbon to conversion at a temperature within the range of about 600° to about 1200° F. in the presence of a catalyst comprising a mechanical mixture of gamma alumina and sublimed molybdic oxide.

4. A hydrocarbon conversion process which comprises subjecting hydrocarbons boiling within the range of gasoline to reforming in the presence of a catalyst comprising a mechanical mixture of porous supporting material and sublimed molybdenum oxide.

5. A hydrocarbon conversion process which comprises subjecting hydrocarbons boiling within the range of gasoline to reforming at a temperature within the range of about 900 to about 1100° F., in the presence of hydrogen and a catalyst comprising a mechanical mixture of gamma aluminum oxide and sublimed molybdic oxide.

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6. A hydrocarbon conversion process which comprises subjecting hydrocarbons boiling above the range of gasoline to cracking in the presence of a catalyst comprising a mechanical mixture of a porous supporting material and sublimed molybdenum oxide.

7. A hydrocarbon conversion process which comprises subjecting hydrocarbons boiling above the range of gasoline to cracking at a temperature within the range of about 800 to about 1000° F., in the presence of hydrogen and a catalyst comprising a mechanical mixture of gamma aluminum oxide and sublimed molybdic oxide.

8. A hydrocarbon conversion process which comprises subjecting said hydrocarbon to dehydrogenation in the presence of a catalyst comprising a mechanical mixture of a porous supporting material and sublimed molybdenum oxide.

9. A hydrocarbon conversion process which comprises subjecting said hydrocarbon to dehydrogenation at a temperature within the range of about 800 to about 1200° F., in the presence of a catalyst comprising a mechanical mixture of gamma aluminum oxide and sublimed molybdic oxide.

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