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HYDROFORMING PROCESS WITH THE ADDITION OF A NITROGENOUS BASE

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This invention pertains to the catalytic conversion of hydrocarbons and more particularly to the catalytic reforming or hydroforming of hydrocarbon fractions boiling within the motor fuel or naphtha range of low octane number into high octane number motor fuels rich in aromatics.

It is known that petroleum naphthas can be subjected to a reforming treatment to yield liquid products boiling within the naphtha or motor gasoline boiling range and possessing improved octane numbers and better engine cleanliness characteristics. A well known and widely used method for upgrading petroleum naphthas is called hydroforming. In hydroforming, the naphtha feed stock is treated at elevated pressures of from 15 to 1000 pounds per square inch and at temperatures of 750°–1050° F. in the presence of solid catalyst particles and hydrogen or recycle gas rich in hydrogen. A variety of reactions including dehydrogenation, paraffin and naphthene isomerization, cyclization or aromatization, hydrogenation and hydrocracking, occur during hydroforming. All these reactions contribute to the production of a motor fuel product of increased value not only because of its higher octane number but also because of its improved cleanliness characteristics due to the elimination of gum-forming unsaturated constituents and the removal of sulfur.

Catalysts that have been used for hydroforming include metals such as platinum and palladium as well as oxides and sulfides of group VI metals, particularly molybdenum, chromium, vanadium, and tungsten. These catalytic components are usually supported upon a base or spacing agent, preferably on an adsorptive or high surface area alumina-containing composition such as various activated aluminas, alumina gel, zinc aluminate spinel, and the like.

In view of the ever-increasing demands for more and higher octane number "premium" motor fuels, a great deal of research has been directed toward the development of new catalysts having increased activity, permitting the charging of greater quantities of feed stock and/or having greater selectivity, thereby yielding greater quantities of final product of high octane number. Much effort has also been directed toward the development of new techniques in the actual conduct of the hydroforming reaction in order to produce greater quantities of the desired high octane products and which may in addition minimize process losses in the form of dry gas formation and the deposition of inactivating carbonaceous products upon the catalyst. Effort has also been directed toward overcoming the adverse effects of certain constituents of the naphtha feed stocks. Sulfur or organic sulfur compounds in naphthas has been particularly troublesome in hydroforming. It has been found, for example, that when a

high sulfur feed is introduced into a hydroforming reaction zone containing a catalyst comprising platinum dispersed upon alumina obtained by hydrolysis of aluminum alcoholate after a considerable period on low sulfur feed with high gasoline yield, there is a considerable drop in activity amounting to as much as 8 to 10 octane numbers.

It is the object of this invention to provide the art with a novel hydroforming process.

It is also the object of this invention to provide the art with a method of carrying out a hydroforming process whereby excessive hydrocracking may be inhibited or prevented.

It is a further object of this invention to provide an improved process of hydroforming naphtha feed stocks of high sulfur content whereby high yields of high octane number products are obtained.

These and other objects will apear more clearly from the detailed specification and claims which follow.

It has now been found that excessive cracking or hydrocracking that occurs in aromatization and hydroforming processes, especially at pressures of 200 pounds per square inch and over, when charging certain sulfur-containing feeds, may be effectively suppressed by introducing small amounts of ammonia or other nitrogenous base such as alkyl or aryl amines or other nitrogen-containing compounds which may be reduced to amino compounds under reaction conditions in the reforming reaction zone. The addition of ammonia or other nitrogenous base is especially advantageous since it suppresses the cracking reaction without simultaneously suppressing the other reactions such as dehydrogenation and cyclization which lead to the formation of aromatics from naphthenes and paraffins. In other words, the addition of a nitrogenous base, preferably ammonia, to a reforming reaction zone serves to minimize dry gas formation while simultaneously maximizing the production of aromatics.

The reforming reaction in accordance with the present invention can be carried out in a fixed-bed, moving bed, or fluidized solids type of operation. The reaction zone is maintained at a temperature of from 800°–1100° F., preferably at about 950° F., and at pressures from atmospheric up to about 1000 pounds per square inch. Different catalyst compositons have different optimum operating pressures. Molybdic oxide or chromic oxide on zinc aluminate spinel are most effective at about 50 pounds per square inch, while molybdic oxide upon an adsorptive alumina support is generally most effective at about 200 pounds per square inch. Platinum on alumina, on the other hand, is effective over a wide pressure range, at about 200–350 pounds per square inch to produce high octane number (90+) products in a regenerative type operation and at pressures above about 400 pounds per square inch in a non-regenerative operation to produce lower octane number products. Hydrogen is circulated through the reaction zone at a rate of from about 2000 to 8000 cubic feet per barrel of liquid naphtha feed. The weight ratio of catalyst to oil introduced into the reactor should be about 0.5 to 3.5, preferably about 1.0. The space velocity or weight in pounds of feed charged per hour depends upon the age or activity level of the catalyst, the character of the feed stock, and the desired octane number of the product. Ordinarily, it may vary from about 0.5 w./hr./w. to 15 w./hr./w.

The catalysts that may be used in the reforming reaction zone may be any of the usual reforming catalysts such as one containing 0.01 to 2.0 weight percent platinum or 0.05 to 5.0 weight percent palladium upon acti-

vated or adsorptive alumina or one containing a group VI metal oxide upon a support such as activated alumina, alumina gel, or zinc aluminate spinel. A particularly effective catalyst of this type is one containing from about 4.0 to 15.0 weight percent molybdic oxide, preferably about 10.0 weight percent, dispersed upon activated or adsorptive alumina.

The nitrogenous bases that can be supplied to the hydroforming reaction zone may be ammonia or amines including arylamines such as aniline or alkyl and alkanol amines such as methyl, ethyl, propyl, ethanolamine, and the like. Ammonia is preferred because it is economical, easy to use, and highly effective. Other compounds that can be used include nitrobenzene, nitrosobenzene, and oximes.

The nitrogenous base may be applied in various ways as by addition to the naphtha feed or to the recycle gas to the process. In either event the amount of ammonia or nitrogenous base is very small and may be applied continuously or intermittently. When applied with the recycle gas or the feed, the amount added may vary from about 1 to about 20, preferably 2–5, parts per million based upon the naphtha fed to the unit.

The naphthas that may be treated in accordance with the present invention are virgin naphthas, cracked naphthas, Fischer-Tropsch naphthas, or mixtures of two or more naphthas having a boiling range of from about 125° F. to about 450° F., or it may be a narrow boiling cut within this broad range. The naphthas treated in accordance with this invention may be termed high sulfur naphthas and are characterized by containing more than about 0.10 weight percent sulfur.

The following examples are illustrative of the present invention.

EXAMPLE I

A virgin naphtha containing 0.21 weight percent of added sulfur (as n-dipropyl sulfide) was hydroformed in contact with a platinum (0.6 weight percent) on alumina catalyst at 915° F., 200 p.s.i.g., and 5000 s.c.f./b. hydrogen rate. At the start of the process the correlated C_5+ gasoline yield at 95 O.N. was 85 volume percent. After about 440 hours on this feed, the correlated C_5+ yield at 95 O.N. had declined to about 80.5 volume percent.

At this stage addition of 7 p.p.m. of ammonia to the feed served to restore the yield to 85 volume percent. This was accompanied by a decline in activity and product octane. Raising the temperature essentially restored the product octane while the higher selectivity was retained. Data from these runs are shown in Table I.

Table I

Hour	440	499	500–540
Ammonia, p.p.m. in Feed	0	7	7
Mid-Sand Temperature, °F	915	915	940
CFR–R Octane No., Clear	96	90	94
C_5+ Yield at 95 O.N., Vol. percent	80.5	85	85

EXAMPLE II

In another experiment, an overdose of ammonia was added. In a life run with a platinum (0.6 weight percent) on alcoholate alumina catalyst the selectivity had dropped from 85 to 79.5 volume percent at 95 octane after 340 hours' operation with a virgin naphtha to which 0.24% S as n-dipropyl sulfide was added. Addition of 200 p.p.m. of ammonia to the feed increased correlated yield to 88% but activity was decreased markedly. When the temperature was increased the octane level was not increased accordingly, indicating that the ammonia had destroyed the activity of the catalyst. The results are shown in Table II.

Table II

Hour	340–380	392	413
Ammonia, p.p.m. in Feed	0	200	200
Mid-Sand Temperature, °F	915	915	950
CFR–R Octane No., Clear	95	78	82
C_5+ Yield at 95 O.N., Vol. percent	79.5	88	87

Based on these experiments, it appears that the optimum amount of ammonia may be below 7 p.p.m. In these examples, the ammonia was added after the catalyst had been on high sulfur feed for several hundred hours. The addition of as little as 2 p.p.m. of ammonia from the very beginning of the run would be effective for improving selectivity, without decreasing activity appreciably.

EXAMPLE III

A virgin naphtha containing 0.15 weight percent sulfur was hydroformed in contact with a platinum (0.6 weight percent) on alcoholate alumina catalyst at 965° F., 500 p.s.i.g., and 6000 s.c.f./b. hydrogen rate and at 12 w./hr./w. space velocity. After the catalyst had lost 7 volume percent correlated C_5+ yield at 85 octane, a small amount of nitrobenzene, which is readily reduced to aniline under reactor conditions, was added to the feed. As with ammonia addition, activity declined and correlated gasoline yield improved. The data obtained are summarized in Table III below.

Table III

Run Hours	955–7	961–6	973–5
Sand Bath Temperature	966	963	965
Nitrobenzene Added, Wt. percent	None	0.012	None
Product Yields and Quality—Total C_5+ Gasoline:			
Yield, Vol. percent on Fresh Feed	86.4	92.2	88.6
CFR Research Octane, Clear	81.4	76.0	79.6
C_4, Vol. percent on Fresh Feed	5.5	3.0	4.6
Dry gas, Wt. percent on Fresh Feed	8.8	4.4	7.2
Yields Correlated to 78 Octane:			
C_5+Gasoline, Vol. percent on Fresh Feed	88.9	91.2	89.2
C_4, Vol. percent on Fresh Feed	4.2	2.0	3.6
Dry Gas, Wt. percent on Fresh Feed	7.2	5.0	6.8

The foregoing description contains a limited number of embodiments of this invention. It will be understood that numerous variations are possible without departing from the scope of this invention.

What is claimed is:

1. In the hydroforming of an initial naphtha feed fraction containing over 0.1 weight percent of sulfur in admixture with hydrogen at conversion conditions of temperature and pressure and in the presence of an active hydroforming catalyst, the improvement which comprises minimizing cracking reactions by adding a nitrogenous base in an amount below 20 parts per million based on naphtha feed to the reaction zone during the hydroforming process, said nitrogenous base being in addition to the nitrogen present in the initial naphtha feed fraction to be reformed.

2. The process as defined in claim 1 in which the catalyst comprises platinum upon an alumina support.

3. The process as defined in claim 1 in which the catalyst is a group VI metal oxide upon an alumina support.

4. In the hydroforming of naphtha fractions containing over 0.1 wt. percent sulfur, in admixture with hydrogen at a conversion temperature and in the presence of an active hydroforming catalyst, the improvement which comprises continuing the conversion of said naphtha until the yield drops below a desired value, then adding a nitrogenous base in an amount below 20 parts per million based on naphtha feed to restore the yield,

and increasing the conversion temperature to restore catalyst activity and product octane.

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