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2,870,084

PROCESS OF AROMATIZING A NAPHTHA WITH AN ALUMINA-CHROMIA-PLATI- NUM CATALYST

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This invention relates to the catalytic conversion of hydrocarbons, and more particularly to catalytic reforming.

In catalytic reforming, relatively light petroleum fractions, such as naphthas and gasolines containing an appreciable amount of paraffins and naphthenes, are treated at an elevated temperature in the presence of a catalyst to alter their characteristics. The reforming reactions embrace dehydrogenation, dehydro-cyclization and aromatization of the hydrocarbons to produce fractions of approximately the same general boiling range, but of different chemical structure and performance characteristics. A reformed product has a substantially increased octane number due in part to the increased aromatic content. Hydrogen is usually formed as one of the products.

When the petroleum fraction is subjected to such a conversion, cracking usually takes place concurrently with the reforming. This apparently results from the fact that catalysts and reaction conditions that promote reforming also promote cracking more or less. It is believed that the cracked products polymerize under the reaction conditions, and that the end product of the polymerization is coke. This coke formation is not primarily a product of the reforming. Rather it is believed that the coke results from the cracking-polymerization reactions which take place concurrently with the reforming. As a result, a deposit of coke is laid down on the catalyst and the rate at which this coke is deposited depends upon the conditions of conversion and upon the catalyst. In general, conditions which give a high conversion level result in increased coke deposit. In most of the usual cases, especially those employing oxide type catalysts, the coke gradually destroys the activity of the catalyst for promoting the desired conversion. This loss in catalyst activity necessitates the regeneration of the catalyst generally by burning off the coke. It is highly desirable, therefore, to provide processes using conditions and a catalyst which will minimize the deposition of coke during the reforming conversion.

This desirability of a minimum coke-producing reforming conversion is economically attractive from the standpoint of savings in capital expenditure for regeneration equipment, or the loss of "on stream" time if the regeneration is done in the same equipment, as well as in savings of feed stock. Particularly is this so when it is desired to operate the process at high conversion levels where coke production ordinarily represents a greater problem.

It has been proposed heretofore to carry out the reforming conversion in the presence of added hydrogen, and it has been found that the excess hydrogen tends to decrease the amount of coke deposited, probably due to the repression of the polymerization reactions. The presence of hydrogen, however, inhibits the reforming reaction to some extent and requires increased temperatures to produce the same quality of product that is produced in the absence of hydrogen at lower temperatures. However, coke formation is not eliminated by

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the use of hydrogen, and the process does not become non-regenerative even at hydrogen partial pressures high enough for near complete repression of the reforming reactions.

Inasmuch as the use of hydrogen cannot completely prevent coke formation and only at best repress it, it is desirable to operate at lower hydrogen partial pressures, and therefore lower total pressures, if other variables can be selected which will give a low coke deposition at the low pressures. Not only is the construction of reaction equipment facilitated by the use of low pressures, but the passage from the reforming to the regenerating cycle is facilitated if the reforming operation is carried out at a low pressure. Regeneration at high pressures is not practical, so that if the reaction pressure is high, complicated equipment, such as locks, must be provided for changing the pressure between the reaction and the regeneration. If the pressure is sufficiently low, the difference between the reaction pressure and atmospheric regeneration pressure can be taken care of in the "fluid" type equipment with a "leg" of catalyst as is well understood in the art.

In accordance with our invention, we have discovered that hydrocarbons may be reformed utilizing a co-precipitated alumina-chromia catalyst containing a small amount of an oxide of platinum or palladium (or both) under reforming conditions using a relatively low hydrogen partial pressure and low operating pressure, to give a much higher level of conversion without any corresponding increase in coke deposition, or from the alternative point of view, a minimization of coke deposition at the conversion levels, as compared with catalysts previously known when operated under the same conversion conditions. In addition, the relatively low hydrogen partial pressures useable with this catalyst provide an optimum yield-octane relation and minimize butane production.

Prior Patent No. 2,236,514, assigned to our assignee, describes a gel-type catalyst of alumina and chromia in the proportions of 70-82 mol percent alumina and 18-30 mol percent chromia formed by co-precipitating precursors of these two ingredients. A preferred embodiment described in the patent consists in co-precipitating a catalyst to provide 80 mol percent alumina and 20 mol percent chromia by treating nitrates of the two metals with ammonia. Catalysts with proportions of the two oxides within the ranges stated may be made by other co-precipitating methods such as the reaction of sodium aluminate with a soluble chromium salt such as chromium nitrate or chromium acetate, with adjustment of the pH up to about 10, if necessary.

Merely as illustrative, such a catalyst may be prepared by mixing solutions of chromium acetate and sodium aluminate in proportions to provide a co-precipitated catalyst having 76 mol percent of alumina and 24 mol percent chromia accompanied by the addition of sulfuric acid to maintain a pH of about 8.5. The catalyst is washed free of sulfate, dried and has 3% volatiles at 1000° F.

This catalyst was used in a reforming operation employing a naphtha having a Kattwinkel number of about 10.5 (A. S. T. M. Standard Method D875-46T which is a measure of olefins and aromatics), an initial boiling point of 222° F., 50% over at 282° F. and an end point of 397° F. The reforming conditions were as follows:

Temperature of conversion	980° F.
Total pressure (gauge)	25 lbs. per square inch.
Hydrogen to naphtha mol ratio	4.9.
Hydrogen partial pressure (ab-	
solute)	33 lbs. per square inch.
Feed rate	1.32 v. v. h.
On stream time	30 minutes.

The reformed product as obtained was analyzed for Kattwinkel number as a measure of the reforming conversion. The catalyst after being flushed with nitrogen and cooled was analyzed for coke by a conventional carbon determination method utilizing combustion in a quartz tube. The following results are typical of the average of a large number of conversions with slight extrapolation to the higher conversion:

Kattwinkel number:	Coke, wt. percent
50	2.2
60	3.4
70	4.5

Kattwinkel numbers in the range of 55 to 65 correspond approximately to octane numbers of 80 to 90 by the F-1 method.

Considering that coke percentages in excess of 3 to 3½% are excessive for a commercial operation, it will be seen that while this catalyst is one of the best available, the extent of the conversion with the permissible coke conversion, has its limits.

It has also been proposed heretofore in Patent Nos. 2,250,415 and 2,410,044 to add a small amount of antimony oxide to such a catalyst as a third component. When a catalyst comprising 73.7 mol percent alumina, 24.6 mol percent chromia, and 1.7 mol percent antimony oxide was used in conversions on the same naphtha and under the same conditions described heretofore, the following results are typical of numerous experiments with slight extrapolation to the upper conversion level:

Kattwinkel number:	Coke, wt. percent
50	1
60	2.2
70	3.3

It will be seen that the conversion level of this catalyst is much higher than those without the antimony oxide and represents one of the best catalysts up to this time that is available for operation under these conditions.

In accordance with our invention we reform hydrocarbon fractions such as naphthas and virgin gasolines, under reforming conditions utilizing a low pressure, and in the presence of a co-precipitated chromia-alumina catalyst impregnated with a relatively small amount of an oxide of platinum or palladium or both. While all three components may be co-precipitated, we find the catalyst entirely suitable when the chromia and alumina are co-precipitated and the third element incorporated by impregnation. The catalyst base may be the same as that described heretofore and may be made by the same methods, i. e., co-precipitation of alumina and chromia within the ranges described heretofore. Catalysts used in the process of the invention may be impregnated with a solution of a salt of platinum or palladium which can be converted to the oxide upon heating. The concentration of the solution and the length of the impregnating time are such as to incorporate the desired amount of the third oxide which may be from 0.001 to about 1.0 mol percent. In general, the catalyst is treated with the solution in a concentration of 0.0001 to 0.10 mol per liter. The catalyst may be treated with the impregnating solution for from a few minutes to several days, depending on the concentration of the solution and the amount to be absorbed, the excess solution drained away, and the catalyst dried. The catalyst is then heated at a high temperature such as 850 to 1250° F. for a period of four to twenty-four hours in an atmosphere of a gas such as dry nitrogen and cooled in the similar atmosphere. During this heating the impregnating element was converted to the oxide.

The catalyst may be in any of the usual physical forms, more particularly, in particles of any size or shape. If the catalyst is finely divided, the reforming operation may be carried out with the catalyst in a "fluidized" condition using the so-called fluid reforming technique. The

catalyst may also be in larger particles, such as beads, which are more commonly used in the fixed and moving bed techniques.

The reforming operation is carried out under any of the usual reforming conditions provided the pressure is relatively low, which is an advantage of our process. In general, the temperature will be between 800 to 1200° F., preferably 900 to 1000° F. The total pressure will be from atmospheric to about 100 pounds, preferably about 25 pounds, per square inch gauge and the conversion conducted in the presence of added hydrogen to provide a hydrogen partial pressure of about 10 to about 85, preferably 10 to 50, pounds per square inch absolute. The rate of feed may be maintained at from about 0.3 to 10 volumes of hydrocarbon feed per volume of catalyst per hour.

The following examples are illustrative of catalysts which may be used in accordance with our invention:

Example 1

A base reforming catalyst having a composition of 76 mol percent alumina and 24 mol percent chromia, co-precipitated as above described, free of sulfate and having 3% volatiles at 1000° F., is impregnated with a solution of palladium chloride in a concentration of 0.09 mol per liter by permitting the catalyst to soak in such a solution in the proportions of 200 pounds of catalyst to 100 of the aqueous solution of the palladium chloride at room temperature for one hour. The excess solution was drained from the catalyst, and it was dried at 300° F. for four hours. The catalyst was then heated for sixteen hours at 1000° F. in an atmosphere of dry nitrogen, cooled in nitrogen and bottled for testing. The catalyst contained 0.5 mol percent palladium oxide.

The same straight-run naphtha as described heretofore was passed through the resulting catalyst under the same conditions described heretofore. The Kattwinkel number of the reformed naphtha was 72 and the coke on the catalyst was 1.82%. This is an unusually high conversion level and the extent of the coke formation is small as compared to the catalysts described heretofore, as can be seen by the following comparison:

Catalyst	Kattwinkel Number	Percent Coke
Al-Cr Oxides	72	4.7
Al-Cr-Sb Oxides	72	3.5
Al-Cr-Pd Oxides	72	1.82

Example 2

The above example was repeated except that the impregnating solution comprised platinum chloride and the amount of platinum oxide in the catalyst was 0.3 mol percent. Using the same naphtha and the same reforming conditions, the reformed product had a Kattwinkel number of 71 and the catalyst had a coke content of 2.55%. While in this example the amount of platinum oxide is half of the amount of palladium oxide in the previous example, the conversion level is nevertheless unusually high and the amount of coke well below amounts under commercial conditions, as is seen from the following comparison:

Catalyst	Kattwinkel Number	Percent Coke
Al-Cr Oxides	71	4.6
Al-Cr-Sb Oxides	71	3.45
Al-Cr-Pt Oxides	71	2.55

It is to be noted that the amount of platinum oxide or palladium oxide is quite small especially as compared with the amount of antimony described in the prior art component catalyst and that the results are attractive considering especially the relatively low hydrogen partial

pressure and its advantages and the high conversion level and low coke formation indicated.

These results are attributed primarily to the addition of the third component oxide to a co-precipitated alumina-chromia base. It appears that the palladium or platinum oxide accomplishes its unusual promoter action because of the intimate association of the oxides comprising the base.

The third component is in the oxide form at the beginning of the reforming operation. It is believed to be in the oxide form after regeneration to burn off coke. During the reforming a part or all of the oxide may be reduced but because of the small amount it is difficult to ascertain the exact form of this component during the entire reforming operation.

It can readily be seen from the preceding discussion that the incorporation of very small amounts of the oxides of the platinum and palladium on an alumina-chromia co-precipitated base catalyst gives a substantial reduction in the rate of coke deposition at low hydrogen partial pressures as compared with the alumina-chromia base catalyst or other three component catalysts heretofore available.

The word "chromia" is used herein synonymously with "chromium oxide."

We claim:

1. A process for catalytically reforming petroleum

naphtha which comprises contacting said naphtha at a temperature in the range of about 800 to 1200° F. at a total pressure of about 0 to 100 p. s. i. g. at a hydrogen partial pressure of about 10 to 80 p. s. i. absolute with a co-precipitated alumina-chromia catalyst having 70 to 82 mol percent alumina, having 30 to 18 mol percent chromia, and containing as a third component an oxide selected from the group consisting of platinum oxide and palladium oxide in the proportions of about 0.001 to 1.0 mol percent based on the weight of the catalyst.

2. A process for catalytically reforming petroleum naphtha which comprises contacting said naphtha at a temperature of about 980° F. at a total pressure of about 25 p. s. i. g. at a hydrogen and at a partial pressure of about 33 p. s. i. absolute with a co-precipitated alumina-chromia catalyst comprising about 75.8 mol percent alumina, about 23.9 mol percent chromia, and about 0.3 mol percent platinum oxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,236,514	Burk et al.	Apr. 1, 1941
2,317,683	Greensfelder	Apr. 27, 1943
2,479,110	Haensel	Aug. 16, 1949
2,635,082	Smith	Apr. 14, 1953
2,678,923	Hansford	May 18, 1954