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PROCESS FOR REFORMING HYDROCARBONS WITH AN ALUMINA-CHROMIUM OXIDE CATALYST CONTAINING EITHER GERMANIUM OXIDE, INDIUM OXIDE, OR GALLIUM OXIDE

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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, dehydrocyclization 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 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 particularly desirable and 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 addition, the relatively low hydrogen partial pressures useable with this catalyst provide an optimum yield-octane relation and minimize butane production.

In accordance with our invention, we have discovered that hydrocarbons may be reformed utilizing a co-precipitated alumina-chromium oxide catalyst containing a small amount of an oxide of germanium, indium and gallium 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. The exact cause of the reduction of coke deposition by the addition of such small amounts of these metal oxides is not fully understood; however, it may be due to the fact that the concurrent and inherent manifestations attributable to cracking or polymerization or both which accompany the reforming conversion are minimized without adversely affecting the reforming.

A surprising fact in connection with these catalysts is that the efficacious reduction in coke deposition does not appear to be a common function of closely related metal oxides functioning as third components which might be expected to show similar properties, but rather appears to be a specific property of certain metal oxides. More particularly, it has been found that when one metal oxide is efficacious for this purpose, others of the same periodic group which might be expected to function similarly do not do so. This is illustrative of the unpredictability of the oxides found to be suitable.

Prior U. S. Patent 2,236,514, assigned to our assignee, describes a gel-type catalyst of alumina and chromium oxide in the proportions of 70–82 mol percent alumina and 18–30 mol percent chromium oxide 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 chromium oxide 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

chromium oxide 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	°F.	980
Total pressure (gauge)		[1] 25
Hydrogen to naphtha mol ratio		4.9
Hydrogen partial pressure (absolute)		[1] 33
Feed rate	v./v./hr.	1.32
On stream time	minutes	30

[1] Pounds per square inch.

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:

Kattwinkel Number	Coke, Wt. Percent
50	2.2
57	3.1
58	3.2
62	3.5

Kattwinkel numbers in the range of 55 to 65 correspond approximately to octane numbers of 80–90 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 chromium oxide, 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:

Kattwinkel Number	Coke, Wt. Percent
50	1.0
57	1.8
58	1.9
62	2.3

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 chromium oxide-alumina catalyst impregnated with a relatively small amount of an oxide of a metal selected from the group consisting of germanium, indium and gallium. 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 oxide 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 chromium oxide within the ranges described heretofore. Catalysts used in the process of the invention may be impregnated with a solution of a salt or other compound of the third named element 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 0.1 to about 2.0 mol percent. Generally there is no advantage in using over 1.0 mol percent and in the following examples good results were obtained with 0.2 to 0.4 mol percent of the third metal oxide. In general, the catalyst is treated with the solution in a concentration of 0.05 to 0.5 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 if it was not previously in that form.

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 50 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 45 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 chromium oxide, co-precipitated as above described, free of sulfate and having 3% volatiles at 1000° F., is impregnated with an ether solution of germanium tetrachloride in a concentration of 0.05 mol per liter by permitting the catalyst to soak in such a solution in the proportions of 2 pounds of catalyst to 0.75 pound of the ether solution of the germanium tetrachloride at room temperature for one hour. The excess solution was drained from the catalyst which was then treated with 1 pound of water to convert germanium tetrachloride to germanium oxide. Excess solution was again drained and the remaining catalyst 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 0.4 mol percent germanium 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 58 and the coke on the catalyst was 1.48%. This represents a reduction in the

coke formation as compared to the catalysts described heretofore, as can be seen by the following comparison:

Catalyst	Amount of Third Component, mol Percent	Kattwinkel Number	Percent Coke
Al-Cr Oxides		58	3.2
Al-Cr-Sb Oxides	1.7	58	1.9
Al-Cr-Ge Oxides	0.4	58	1.48

Example 2

Two pounds of the catalyst base used in Example 1 were impregnated with 1 pound of an aqueous solution containing 0.045 mol per liter of indium nitrate. The drying procedure of Example 1 was then repeated. The amount of indium oxide in the catalyst was 0.2 mol percent. Using the same naphtha and the same reforming conditions, the reformed product had a Kattwinkel number of 57 and the catalyst had a coke content of 1.41%. The conversion level is satisfactory and the amount of coke well below amounts obtained when the other catalysts are used, as is seen from the following comparison:

Catalyst	Amount of Third Component, mol Percent	Kattwinkel Number	Percent Coke
Al-Cr Oxides		57	3.1
Al-Cr-Sb Oxides	1.7	57	1.8
Al-Cr-In Oxides	0.2	57	1.41

Example 3

Two pounds of the catalyst base used in Example 1 was treated with 1 pound of aqueous solution containing 0.07 mol per liter gallium nitrate. The drying procedure was the same as in the previous examples. The amount of the gallium oxide in the catalyst was about 0.4 mol percent. Using the same naphtha and the same reforming conditions, the reformed product had a Kattwinkel number of 50 and the catalyst had a coke content of 1.1%. The catalyst compares favorably in results with the catalyst described heretofore promoted by antimony, but the amount of the third component to achieve this result is substantially less. This can be seen from the following table:

Catalyst	Amount of Third Component, mol Percent	Kattwinkel Number	Percent Coke
Al-Cr Oxides		50	2.2
Al-Cr-Sb Oxides	1.7	50	1.0
Al-Cr-Ga Oxides	0.4	50	1.1

It is to be noted that the amount of third component 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.

It can be readily seen from the preceding discussion that the incorporation of very small amounts of the oxides of the third components 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-chromium oxide base catalyst or other three component catalysts heretofore available.

We claim:

1. The process for reforming petroleum fractions which comprises contacting said fractions under reforming conditions including hydrogen to provide a partial pressure of 15–45 pounds per square inch absolute in the presence of a co-precipitated alumina-chromium oxide catalyst consisting of alumina, chromium oxide, and a small proportion of a third component oxide selected from a group consisting of germanium oxide, indium oxide and gallium oxide.

2. The process of claim 1 in which the co-precipitated alumina-chromium oxide are in the proportions of 70–82 mol percent alumina to 30–18 mol percent chromium oxide, and in which the oxide of the third component is present in the proportions of 0.1 to 2.0 mol percent.

3. The process of claim 1 in which the reforming operation is carried out at a temperature of about 980° F. at a total pressure of about 25 pounds per square inch gauge, at a hydrogen partial pressure of about 33 pounds per square inch absolute, with a catalyst consisting of about 75.8 mol percent alumina co-precipitated with about 23.8 mol percent chromium oxide, and about 0.2 to 0.4 mol percent of the oxide of the third component.

4. The process of claim 2 in which the catalyst is finely divided and the reforming is carried out with the catalyst in a fluidized form.

References Cited in the file of this patent

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