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REFORMING PROCESS AND CATALYSTS

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This invention relates to the catalytic conversion of hydrocarbons and particularly to reforming of hydrocarbons. More particularly, this invention relates to catalysis and hydrocarbon conversion in the presence of a novel catalyst.

It is well known that in the treatment of hydrocarbons in which there is a scission of the carbon-to-carbon and hydrogen-to-carbon bonds in the presence of catalytic material there is a relatively heavy deposit of coke laid down upon the catalytic material. The rate at which this coke is deposited depends upon the conditions of conversion but in all cases the layer of coke progressively destroys the activity of the catalytic material in promoting the conversion of the hydrocarbon. The rate at which the catalytic activity is destroyed is dependent upon the rate at which the coke is deposited upon the catalytic material. This loss in catalytic activity necessitates the regeneration of the catalytic material by removal of the coke. It is highly desirable to obtain processes and catalysts which will minimize the deposition of coke during hydrocarbon conversions.

In hydrocarbon conversions designated as reforming, relatively light petroleum fractions such as naphthas and gasolines are treated under elevated temperature and pressure to alter the characteristics of the petroleum product. Reforming embraces substantial dehydrogenation and aromatization of the hydrocarbons to products of approximately the same boiling range but of different characteristics. Hydrogen is formed as one of the products. An advantage of reforming is the substantial increase of octane rating of the reformed product.

Cracking of the petroleum fraction in varying amounts usually takes place concurrently with the reforming conversion. This results from the fact that catalysts and reaction conditions which promote reforming also promote cracking, more or less. Varying amounts of coke are deposited during the reforming process depending upon the conditions of the conversion. The coke is not primarily a product of the reforming, but rather results from the polymerization of cracked products which takes place concurrently with the reforming and the cracking.

In a particular method of reforming of hydrocarbon materials in the presence of hydrogen, it has been found that excess hydrogen tends to decrease the amount of coke deposited on the catalytic material. The presence of the hydrogen in the process does not materially alter the overall effects obtained in reforming reaction. The

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reforming is still essentially one of dehydrogenation with a net production of hydrogen and there is considerable aromatization.

In other words, the excess hydrogen represses the coke formation by repressing the polymerization of the cracked products without interfering with the reforming. Coke formation, however, is not eliminated, and the deposition of coke on the catalyst requires regeneration of the catalyst.

The catalysts usually used in reforming comprise certain combinations of metals and metallic oxides. While the oxide type catalysts are effective in reforming operations, most of them cause various amounts of coke deposition on the catalyst material as explained heretofore. Even the use of excess hydrogen in the reforming operation and the use of various catalytic oxide materials have not been effective to eliminate satisfactorily the deposition of coke during reforming operations, and there is still a need for improved catalyst materials which will cause a lower rate of coke deposit.

We have found that when very small amounts of certain metal oxides are incorporated with otherwise known oxide type reforming catalysts, the rate of coke deposition on the catalyst material is substantially reduced. 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 attributed to the cracking, which accompany the reforming conversion, are minimized. It is found that the addition of these metal oxides to the reforming catalyst does not reduce the rate and extent of 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 all related metal oxides that might be expected to show the same property but rather appears to be a specific property of certain metal oxides. That is, it is found that all the metal oxides of a particular class do not show a noticeable decrease in coke formation that certain metal oxides display, as will be brought out more fully below. This is an example of the unpredictability of all chemical properties of related elements.

Some of the more common reforming catalysts are composed primarily of alumina and chromia. Various other metals and metal oxides can be incorporated with these basic metals in the formation of reforming catalysts which are com-

monly used in conversion of various hydrocarbon fractions such as naphthas and other fractions as is well known in the prior art. Examples of such suitable reforming catalysts are disclosed in United States Patents Nos. 2,250,415 and 2,410,044 both to Burk et al. which disclose three-component catalysts which, among others, consist essentially of about 10-30% chromia, 50-90% alumina and 1-30% antimony oxide.

It is found that when small amounts of the order of 0.1-5 mol per cent, preferably 0.3-3 mol per cent, of the oxides of gallium, cadmium, thorium, zirconium, or iridium are incorporated with reforming catalysts of the above type, a substantial decrease in the deposition of coke during reforming operations is obtained. Tests on other related metal oxides which would ordinarily be expected to have a similar property do not show the same noticeable improvement at the concentrations employed. The base reforming catalyst with which the above metal oxides may be incorporated can be prepared by conventional means such as by the co-precipitation from solution of the appropriate salts, or made in any other way that brings the three oxides into intimate mixture. The additional components may be added thereto by impregnating the base catalyst with a solution of a suitable metal salt which can be decomposed thermally to give the desired metal oxide component. Alternatively all four components may be co-precipitated. The base catalysts were found to absorb about 100 ml. of aqueous solution per 100 grams of base catalysts. The impregnating solution concentration used was prepared to contain between 0.1 to 5-gram atoms of the impregnating metallic element per 100 ml. of solution. The base catalysts and the impregnating solution were mixed and the base catalysts allowed to fully absorb the impregnating solution. The excess solution was drained from the base catalyst and the catalyst maintained at elevated temperatures in an atmosphere of dry nitrogen in order to remove the water and thermally decompose the impregnating salt to form the oxide, after which it was cooled under nitrogen and tested.

The hydrocarbon conversion can be carried out under reforming or hydroforming conditions. In general the temperature will be between 800 and 1200° F. and the pressure between atmospheric and 500 lbs. per square inch. The rate of feed may be maintained between 0.3 and 10 volumes of hydrocarbon feed per volume of catalyst per hour and the conversion may be conducted in the presence of .1 to 10 mols of hydrogen per mol of naphtha, to give a hydrogen partial pressure of 0 to 400 p. s. i. g.

The amount of olefins and aromatics in petroleum products is determined using the Tentative Standard testing method which is designated as the A. S. T. M. Standard method D875-46T. This amount is hereinafter referred to as the Kattwinkel number. The difference between the Kattwinkel numbers of the feed stock and the reformed product is indicative of the extent of conversion.

In the examples which follow, comparative tests were run with the base catalyst without the added components of the present invention. After each test the conversion chamber was swept with nitrogen to remove residual conversion products and the catalyst was removed from the reactor. The catalyst was thoroughly mixed and a representative sample analyzed for coke in a quartz tube at 1200 to 1300° F. The combustion gases were ana-

lyzed for CO₂ by standard methods in which the CO₂ is selectively absorbed in a suitable alkaline solution which is then titrated back in the presence of an indicator.

The following examples are illustrative of the preparation of various component catalysts of the present invention and their utility in the conversion of hydrocarbon. The examples, however, are not to be construed as limiting on the scope of the disclosure.

Example 1.—A base reforming catalyst having a composition of 24.6 mol per cent chromia, 73.7 mol per cent alumina, and 1.7 mol per cent antimony oxide was impregnated with a solution of gallium nitrate prepared by dissolving 0.5 gram gallium metal in concentrated nitric acid. The gallium nitrate solution was made up to 200 cc. and mixed with 200 grams of the base catalyst. After all of the solution was absorbed, the resulting material was dried in air at 300° F. for 4 hours. It was then heated for 16 hours at 1000° F. in an atmosphere of nitrogen and cooled in an atmosphere of nitrogen.

Straight-run naphtha boiling between 222 and 397° F. with a gravity of 0.748 at 60° F. and a Kattwinkel number of 10 was passed through the resulting compounded catalyst at a rate of 1.32 volumes of naphtha per volume of catalyst per hour at a temperature of 980° F. and a pressure of 25 lbs. per square inch gauge for an on-stream time of 30 minutes in the presence of 4.9 mols of hydrogen per mol of naphtha feed. The Kattwinkel number of the reformed naphtha was 60. The compound catalyst contained 0.4 mol per cent of gallium and the amount of coke deposited was 0.85% by weight. This compares with a value of approximately 2 weight per cent coke deposition with the base catalyst at the same conversion level to give a Kattwinkel number of 60.

Example 2.—The base catalyst of Example 1 was impregnated with 2.0 mol per cent of cadmium oxide which is effected by impregnating 200 grams of base catalyst with a solution composed of 15.4 grams of cadmium nitrate dissolved in 200 cc. of water. The base catalyst was left in contact with the cadmium nitrate solution for an hour and the excess solution drained off. The resulting material was dried at 300° F. for 4 hours in air and then heated for 16 hours at 1000° F. and cooled in an atmosphere of nitrogen.

The straight-run naphtha of Example 1 was contacted under the same conditions with this compound catalyst and the reformed naphtha was found to have a Kattwinkel number of 62. The amount of coke deposited on the catalyst was 1.49% by weight, which is considerably less than coke deposition with base catalyst without the addition of cadmium.

Example 3.—The base catalyst of Example 1 was impregnated with 2.0 mol per cent of thorium oxide which was incorporated with the base catalyst by mixing 200 cc. of aqueous thorium nitrate solution containing 27.61 grams of thorium nitrate. 200 grams of catalyst were treated with the solution for one hour and the excess solution drained off. The resulting material was dried in air at 300° F. for 4 hours. The material was then heated for 16 hours at 1000° F. and cooled in an atmosphere of nitrogen. The naphtha of Example 1 was treated with this component catalyst under the conditions given in Example 1 and the reformed naphtha was found to have a Kattwinkel number of 60. The coke deposited was 1.49 weight per cent as compared with ap-

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proximately 2 weight per cent for the same level of conversion in the absence of the thorium oxide metal.

Example 4.—The base catalyst of Example 1 was impregnated with 2.0 mol per cent of zirconium oxide which was added by mixing the base catalyst with 200 cc. of aqueous solution containing 13.4 grams of zirconium nitrate. 200 grams of catalyst was treated with this solution for an hour and the remaining solution drained off. The resulting material was dried in air at 300° F. for 4 hours and then heated for 16 hours at 1000° F. and cooled in an atmosphere of nitrogen. When the same naphtha of Example 1 was treated under the identical conditions of conversion, the resulting reformed naphtha had a Kattwinkel number of 62 and the weight per cent of coke deposited was 1.68.

Example 5.—The base catalyst of Example 1 was impregnated with 0.3 mol per cent of iridium oxide which was added by mixing 200 grams of catalyst for one hour with 100 cc. of solution containing 1.5 grams of iridium chloride. All of the solution was absorbed and the resulting material was dried at 300° F. for 4 hours. It was then heated for 16 hours at 1000° F. and then cooled in an atmosphere of nitrogen. The resulting catalyst was contacted with the naphtha of Example 1 under the conditions given therein and the resulting reformed naphtha was found to have Kattwinkel number of 62. The coke deposited amounted to 1.73 weight per cent.

The results of the different tests are given in the following table. The feed stocks are identical and the Kattwinkel number is that of the reformed product. It is seen from the results of the tests that the catalysts which contain a small amount of the metal oxides of the present invention, incorporated with the base catalyst, show a substantial improvement in the rate of coke formation when compared with the base catalyst at the same level of conversion.

Cr-Al-Sb Catalyst		Coke, Wt. Per- cent	Kattwinkel No.
4th Com- pound	Mol Per- cent		
---	---	2.2	60
Ga	0.4	0.85	60
Th	2.0	1.49	60
---	---	2.1	62
Cd	2.0	1.49	62
Zr	2.0	1.68	62
Ir	0.3	1.73	62
---	---	2.9	64
Th	0.4	2.42	64

The foregoing results show the advantageous improvements realized by incorporating one of the metals of the present invention with well-known reforming and aromatization catalysts composed of chromia, alumina and antimony oxide. Data on the coke deposition using the catalyst, both with and without a fourth component of the present invention, are compared for reforming operations at different conversion levels and similar conversion conditions. In this manner the results and improvement can be readily observed. It can be seen that such a decrease in the rate of coke formation is highly desirable in making it possible to employ the catalytic metal oxides for longer periods of conversion before it becomes necessary to stop the conversion and regenerate the catalyst.

It is not expressed that each of the desirable materials proposed in the present invention are

of equal effect in causing a decrease in the rate of coke formation when impregnated on various base reforming catalysts. In fact, it seems that gallium oxide is more effective in producing the desired effect than the other materials; however, it is found that the oxides of thorium, cadmium, zirconium and iridium are also effective in producing the beneficial effects of the invention.

It can readily be seen from the preceding illustrative examples that the incorporation of relatively minor amounts of the oxides of gallium, cadmium, thorium, zirconium, and iridium gives a desirable conversion of hydrocarbons with a substantial reduction in the rate of coke deposition over that obtained with a catalyst in the absence of these materials and at a comparative conversion level. Although in some instances the reduction in the rate of coke deposition does not appear to be large, it becomes a substantial difference when the total deposition of coke per day is considered. The examples have purposely been made using the same base catalyst, the same conversion conditions, and the same feed stock in order to obtain data which will have common basis for comparison. It will be understood that other reforming catalysts and other feed stocks and conditions will show similar improvements when reformed in the presence of catalysts which have small amounts of the metal oxides of this invention incorporated therewith.

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

Various changes and modifications may be in the invention as discussed herein and it is understood that it is intended to include all such modifications and changes as are inherent with the scope of the present invention as discussed and hereinafter claimed. As far as is known, the catalyst claimed has no use other than in the process claimed.

We claim:

1. A process for reforming petroleum fractions which comprises contacting said fractions under reforming conditions with a reforming catalyst containing between 10 and 30 mol per cent chromia, between 50 and 90 mol per cent alumina and between 1 and 30 mol per cent antimony oxide and a minor amount between 0.1 and 5.0 mol per cent of a metal oxide of a metal from the group consisting of gallium, cadmium, thorium, zirconium and iridium.

2. The process of claim 1 in which said petroleum fraction is a naphtha.

3. The process of claim 2 in which said naphtha is reformed in the presence of hydrogen at a temperature between about 800 and 1200° F. and a hydrogen partial pressure up to 400 pounds per square inch.

4. The process of claim 1 in which said metal oxide is present in an amount between 0.3 and 3 mol per cent of the catalyst.

5. The process of claim 4 in which the additional metal oxide is gallium oxide at a concentration of about 0.4 mol per cent of the catalyst.

6. The process of claim 4 in which the additional metal oxide is cadmium oxide at a concentration of about 2.0 mol per cent of the catalyst.

7. The process of claim 4 in which the additional metal oxide is thorium oxide at a concentration of about 2.0 mol per cent of the catalyst.

8. The process of claim 4 in which the additional metal oxide is zirconium oxide at a concentration of about 2.0 mol per cent of the catalyst.

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9. The process of claim 4 in which the additional metal oxide is iridium oxide at a concentration of about 0.3 mol per cent of the catalyst.

10. A catalyst which consists essentially of a chromia-alumina type catalytic material containing between 10 and 30 mol per cent chromia, between 50 and 90 mol per cent alumina and between 1 and 30 mol per cent antimony oxide and a minor amount between 0.1 and 5.0 mol per cent of a metal oxide of a metal from the group consisting of gallium, cadmium, thorium, zirconium and iridium.

11. A catalyst according to claim 10 in which the fourth component is gallium oxide in about 0.4 mol per cent.

12. A catalyst according to claim 10 in which the fourth component is cadmium oxide in about 2.0 mol per cent.

13. A catalyst according to claim 10 in which

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the fourth component is thorium oxide in about 2.0 mol per cent.

14. A catalyst according to claim 10 in which the fourth component is zirconium oxide in about 2.0 mol per cent.

15. A catalyst according to claim 10 in which the fourth component is iridium oxide in about 0.3 mol per cent.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,250,415	Burk et al.	July 22, 1941
2,374,404	Ahlberg	Apr. 24, 1945
2,402,854	Thomas	June 25, 1946
2,410,044	Burk et al.	Oct. 29, 1946