Nov. 12, 1957 E. C. HUGHES ET AL 2,813,114

OXIDATION OF HYDROCARBONS AND OXYGEN CARRIER THEREFOR

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FIG.1.

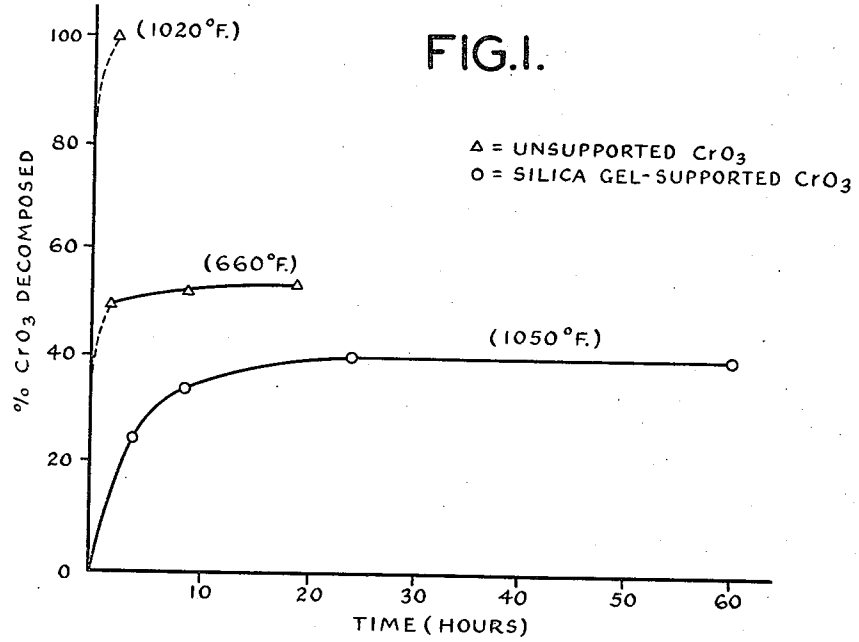
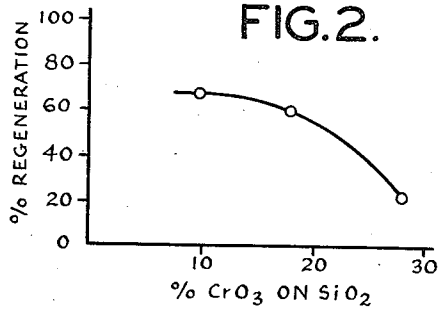


FIG.2.



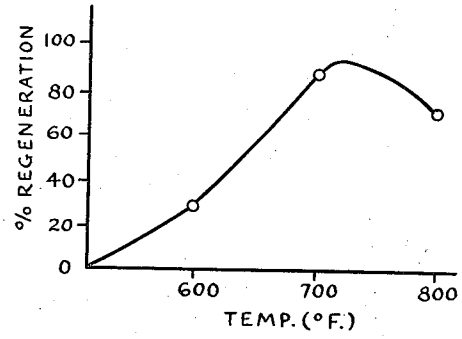


FIG.3.

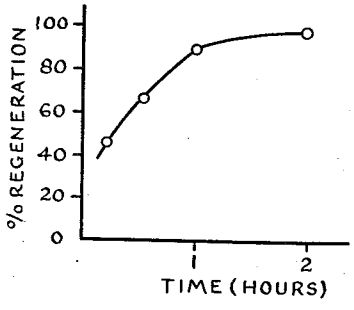


FIG.4.

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OXIDATION OF HYDROCARBONS AND OXYGEN CARRIER THEREFOR

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3 Claims. (Cl. 260—451)

The present invention relates to a process for the reforming of hydrocarbons by partial oxidation.

The petroleum industry has devised many processes for the reforming of hydrocarbons, one type of which is classed as oxidative reforming. In general, oxidative reforming processes are characterized by the reforming of a hydrocarbon in the presence of oxygen or a substance capable of liberating oxygen. In one species of oxidative reforming, the hydrocarbon is contacted with an oxygen-containing gas, such as air, at an elevated temperature. In another species of oxidative reforming, the hydrocarbon is contacted with a metallic oxide in the absence of any added quantities of air or an oxygen-containing gas under conditions which liberate oxygen from the metallic oxide. In the latter species of oxidative reforming, the main reaction which occurs is one between the oxygen of the metal oxide and the hydrocarbon although slight catalytic effects are also present. The oxidation of a hydrocarbon using a solid oxygen carrier offers several advantages over oxidation in the presence of an oxygen-containing gas since the problem of separating the product from the reactants when both include fixed gases is eliminated and, in addition the reaction occurs at a lower temperature, thereby eliminating side reactions such as cracking.

The present invention is concerned with the latter species of oxidative reforming, i. e., the reforming of a hydrocarbon in the absence of an added oxygen-containing gas but in the presence of a metal oxide which will liberate oxygen under the conditions of the reaction.

The latter species of oxidative reforming is illustrated in U. S. Patents Nos. 1,836,325 and 1,836,326 to J. H. James. In the James process, the metal oxide used as an oxygen carrier may be an oxide of titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, tantalum, tungsten or uranium. The oxide can be used as a finely divided material in a fluidized type of process or can be enclosed between screens or similar supports in a fixed bed type of process.

When chromium trioxide is utilized in a process of the type described by James, the liberation of oxygen is known to proceed according to the following equation:

$$4CrO_3 \underset{1020^\circ\ F.}{\overset{2190^\circ\ F.}{\rightleftharpoons}} 2Cr_2O_3 + 3O_2$$

Of the two valence states represented in the formula, the trivalent oxide of chromium (Cr_2O_3) is thermodynamically stable at temperatures below about 1000° F. The hexavalent chromium trioxide decomposes quantitatively to trivalent chromic oxide at about 1020° F. but the reverse reaction does not take place below about 2190° F. From the equation, it is apparent that chromium trioxide in the ordinary case is not readily adaptable as an oxygen carrier for the production of oxygen because excessively high temperatures are required for regeneration from the reduced form.

It is a primary object of the present invention to provide a process for the oxidative reforming hydrocarbons which does not require regeneration temperatures as high as those required in prior art processes.

The above object and others are achieved by a process utilizing chromium trioxide deposited on silica gel as an oxygen carrier in the oxidative reforming process. In essence the process of the invention comprises contacting a hydrocarbon in the vapor phase at an elevated temperature in the absence of an added oxygen-containing gas with an oxygen carrier composed of chromium trioxide deposited on silica gel to reduce the chromium trioxide and reform the hydrocarbon, recovering the reformed hydrocarbon, and regenerating the reduced oxide of chromium by heating in the presence of an oxygen-containing gas such as air.

In accordance with the present invention, it has been found that when chromium trioxide is deposited on silica gel, the thermostability of the chromium trioxide is increased to such an extent that the chromium can easily be reduced to an intermediate valence state less stable than trivalent chromium. The meta-stable system that results from depositing chromium trioxide on silica gel can be represented by the following equation:

$$6CrO_3 \underset{}{\overset{600\text{–}800^\circ\ F.}{\rightleftharpoons}} 2Cr_2O_3.CrO_3 + 3O_2$$

While the precise structure of the reduced oxide on the right hand side of the equation is not known, the average valence of four, as indicated by the formula, has been determined. From the equation, it is apparent that only relatively low temperatures which do not widely differ are required in both the reduction and regeneration steps. The extent to which the reaction will proceed in either direction is largely dependent upon the concentration of oxygen in the surrounding atmosphere. Thus, in accordance with the general laws of chemistry, a high concentration of oxygen will shift the equilibrium toward the left in the above equation whereas, when the concentration of oxygen is low, the equilibrium will shift toward the right.

The successful operation of the process of this invention is subject to criticalities in the temperatures employed for reduction, i. e. oxidation of the hydrocarbon, and regeneration and in the amount of chromium trioxide relative to the silica gel in the oxygen carrier. The temperature employed in the reduction step is perhaps the least critical but it should be within the approximate range of 300 to 950° F. Temperatures below this range do not result in significant improvement of the hydrocarbon and temperatures above the range lead to an undesirable amount of decomposition of the chromium trioxide to the difficulty oxidizable Cr_2O_3, thus interfering with the ease of regeneration.

The temperature of regeneration should be within the approximate range of 600 to 800° F. The percent regeneration at temperatures below 600° F. is too low for satisfactory operation, and above 800° F. irreversible decomposition of the intermediate oxides to Cr_2O_3 results at an increasing rate. Optimum regeneration is obtained within the range of 700 to 750° F. The time of regeneration can be materially decreased by application of superatmospheric pressure but regeneration will proceed satisfactorily at atmospheric pressure.

The amount of chromium trioxide deposited on the silica gel should be limited to 25% by weight because concentrations higher than 25% lead to poor yields in regeneration due to irreversible decomposition of the chromium trioxide. The concentration of chromium trioxide may, however, be as low as desired without encountering irreversible decomposition.

The oxygen carriers employed in the practice of this

invention may be produced in accordance with procedures well known in the art. The preferred procedure involves the impregnation of silica gel with a solution of a chromium compound followed by evaporation of the solvent to yield a dry solid and thereafter converting the chromium compound to the trioxide by heating in air. Alternatively, the silica gel may be impregnated directly with a solution of chromium trioxide in which case conversion to the oxide form is unnecessary.

This invention and the advantages thereof will be described in connection with the attached drawings wherein:

Figure 1 is a graph comparing the percent decomposition into Cr_2O_3 of unsupported chromium trioxide and silica gel-supported chromium trioxide, when heated at atmospheric pressure;

Figure 2 is a graph on which is plotted percent regeneration vs. the percentage by weight of chromium trioxide in the oxygen carrier;

Figure 3 is a graph on which is plotted percent regeneration vs. temperature employed in the regeneration at atmospheric pressure of a silica gel-supported chromium oxide obtained by reduction of chromium trioxide supported on silica gel;

Figure 4 is a graph on which is plotted percent regeneration vs. time in hours for the regeneration of a silica gel-supported chromium oxide at atmospheric pressure.

The data for the decomposition curve on unsupported chromium trioxide for Figure 1 was obtained from the literature, Nargund and Watson, J. Ind. Inst. Sci., 9A, 149 (1926). The data for the decomposition curve on silica gel-supported chromium trioxide for Figure 1 was determined experimentally. It can be observed from Figure 1 that unsupported chromium trioxide readily decomposes to Cr_2O_3 even at temperatures as low as 660° F. On the other hand, silica gel-supported chromium trioxide is relatively stable as regards decomposition to Cr_2O_3. At 1050° F. the decomposition of the supported oxide is less than the decomposition of the unsupported oxide at 660° F., and at temperatures lower than 1050° F. the decomposition of the supported oxide is almost negligible.

The data for Figure 2 was obtained by blowing air at a temperature of 800° F. for one hour through beds of reduced silica gel-supported chromium oxide containing various weight percentages of chromium oxide. It can be observed from Figure 2 that the percent regeneration begins to drop sharply as the concentration exceeds 20% and that about 25% by weight is the upper limit for reasonably efficient operation. Lower concentrations of oxide are not harmful but, for practical reasons, it is desirable to employ as high a percentage of oxide as possible without exceeding 25% by weight. A lower limit of about 10% by weight of the oxide is suggested.

The curve of Figure 3 was obtained by blowing air at various temperatures through beds of a silica gel-supported chromium oxide obtained by the reduction of silica gel-supported chromium trioxide. The ratio of chromium oxide to silica gel was approximately 1 to 9 and the regeneration was carried out in each instance for a period of one hour. From the graph it is apparent that maximum regenerating efficiency is obtained in the range of about 700 to 750° F. When the temperature of regeneration exceeds 800° F. there occurs irreversible decomposition of the intermediate oxides to Cr_2O_3 at an increasing rate, and therefore 800° F. represents a fairly critical upper limit for the regeneration temperature. As the temperature of regeneration falls below 700° F., the efficiency of regeneration drops sharply, and at 600° F. the percent regeneration is approximately 30%. Therefore, 600° represents the approximate minimum temperature of regeneration which can be employed at atmospheric pressure to obtain reasonably satisfactory efficiency in the regeneration step.

Figure 3 further reveals that a maximum regeneration of almost 85% can be achieved by blowing heated air at atmospheric pressure through the reduced oxyen carrier.

Other tests have shown that the same approximate level of regeneration can be achieved through several cycles and the maximum number of cycles through which the oxygen carrier will remain effective appears to be extremely large.

The experiments on which the curve of Figure 4 is based were performed by blowing air for different periods of time through beds of a silica gel-supported chromium oxide which was obtained by the reduction of silica gel-supported chromium trioxide in which the weight ratio of silica gel to chromium trioxide was 8 to 2. The temperature of regeneration in each experiment was 750° F. From the curve of Figure 4 it is apparent that maximum efficiency of regeneration is approached after a period of one hour and that little benefit is realized by regeneration times longer than one hour, although longer times are not harmful and may be used if desired. The shortest regeneration period which can be employed to give a practicable operation of the process at atmospheric pressure is in the neighborhood of ten minutes.

The manipulative steps of the process of the invention are conventional. Any of the various types of reactors which are utilized in the vapor phase processing of hydrocarbons can be employed. Either a fixed bed reactor or a fluid type catalytic reactor is suitable but since fluidized reactions are generally advantageous, it is preferable to carry out the process under fluidized conditions.

In order to further illustrate the process and its accompanying advantages, the following examples are given. Parts and percentages are by weight unless otherwise specified.

Example 1

Forty-seven (47) parts of a commercial silica gel was added to an aqueous solution of 3 parts by weight of chromium trioxide (CrO_3) in 50 parts of water. The resulting mixture was dried for several hours in an oven at 290° F. to yield a granular solid material containing 6% of chromium trioxide.

There was obtained a quantity of a straight-run naphtha having the following properties:

Kattwinkel No.	10.5
Bromine No.	1.4
Gravity (° API)	57.7
Boiling range (° F.)	222–397
Average molecular weight	124

The apparatus employed in the example resembled a conventional fluidized bed catalytic reactor. It consisted essentially of a hopper to contain the solid oxygen carrier, a valve to control the flow of solid into the reaction zone, a reactor with conventional facilities for vaporizing and introducing the hydrocarbon, a vapor solids separator, a solids receiver, a hydrocarbon recovery system and a regenerating vessel for the oxygen carrier. Nitrogen pressure equivalent to 2 to 3 centimeters of mercury was maintained on the feed hopper to insure even flow of the solid and to prevent hydrocarbon vapor from entering the feed hopper.

A quantity of the naphtha was oxidized in the reactor at a temperature of 875° F. using a weight ratio of oxygen carrier to naphtha of 13.6:1. The spent oxygen carrier was then transferred to the regenerator and regenerated with hot air at a temperature of 750° F.

The oxidized naphtha from the reactor was collected in a liquid state in the cooled receiver and the yield of liquid product was found to equal 83% of the naphtha charged. The liquid was analyzed for Kattwinkel number which was found to be 13, an increase of 2.5 over the original naphtha. Since the Kattwinkel number of a hydrocarbon is the measure of the sum of the aromatics, olefins and oxygenated compounds present, it is apparent that the process of the invention results in the formation of a significant amount of oxidized products, olefinic and aromatic compounds. As a result of these chemical

changes in the charge stock, the octane properties are considerably improved.

Example 2

An oxygen carrier was prepared according to Example 1 except that in the preparation 41.5 parts of commercial silica gel was added to an aqueous solution of 8.5 parts of chromium trioxide in 50 parts of water. The oxygen carrier prepared in this manner analyzed about 17.2% chromium trioxide.

The oxidation of the naphtha was carried out at 930° F. by a procedure similar to Example 1 employing a weight ratio of oxygen carrier to naphtha of 5.3:1. The liquid product collected amounted to 83% of the original naphtha charged to the reactor and the product was found to have a Kattwinkel number of 13. Again a significant improvement in the octane number of the naphtha was realized.

The oxygen carrier was regenerated as before by hot air at a temperature of about 750° F.

It is intended to cover all changes and modifications in the examples of the invention, herein given for purposes of disclosure, which do not constitute departure from the spirit and scope of the appended claims.

We claim:

1. In a process for the oxidative reforming of hydrocarbons, the steps of heating to a reforming temperature within the range of 300 to 950° F., materials consisting

essentially of a hydrocarbon and an oxygen carrier comprising a preformed silica gel impregnated with chromium trioxide, the amount of chromium trioxide not exceeding about 25% by weight of the oxygen carrier, thereby reducing the chromium trioxide to a lower oxide down to but not including chromic oxide and reforming the hydrocarbon by the formation of oxidized products, olefins, and aromatics; recovering the reformed hydrocarbons; and reoxidizing the reduced chromium oxide to chromium trioxide by heating in the presence of an oxygen-containing gas at a temperature of from about 600 to 800° F.

2. A process according to claim 1 in which the process is operated continuously with alternate periods of reduction and reoxidizing.

3. An oxygen carrier consisting of chromium trioxide deposited on silica gel, the amount of chromium trioxide not exceeding about 25% by weight of the oxygen carrier.

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