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HYDROCARBON CONVERSION

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This invention relates to the catalytic dehydrogenation of normally liquid hydrocarbons. More particularly, the invention relates to the conversion of aliphatic hydrocarbons having at least six carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof.

Chromium oxide is an active catalyst for the conversion of aliphatic hydrocarbons to aromatic hydrocarbons by dehydrogenation and cyclization thereof. A particularly active form of chromium oxide for this reaction is prepared by the formation of a chromium oxide gel which can be converted to a relatively dense granular material by such washing steps as may be required by reason of the method of preparation of the gel and by suitable drying.

In the conversion of aliphatic hydrocarbons to aromatic hydrocarbons by contact thereof with a gel-type chromium oxide catalyst the hydrocarbon vapors are passed over the catalyst at a temperature in the range of 325 to 650° C., preferably 400 to 550° C. at atmospheric, or higher, pressure. The hydrocarbons are passed over the catalyst at a space velocity which may be varied in accordance with other operating conditions but should be sufficiently low to produce a liquid product containing a substantial proportion of aromatic hydrocarbons. High rates of conversion of aliphatic hydrocarbons to aromatic hydrocarbons are associated with low space velocities and high reaction temperatures, and vice versa. At low temperatures within this range, therefore, a low space velocity may be employed while at higher temperatures a higher space velocity may be used, although these factors are governed also by the character of the material treated and the nature of the product desired. In general the space velocities employed fall within the range of 0.1 to 3 volumes of aliphatic hydrocarbons (liquid basis) per volume of catalyst space per hour. The most advantageous space velocities will be found in the range of 1 to 2 volumes of liquid per volume of catalyst per hour.

In the conversion of aliphatic paraffinic hydrocarbons to aromatic hydrocarbons by contact with a gel-type chromium oxide catalyst under the preferred conditions defined above it is found that when these conditions are controlled to effect production of a substantial proportion of aromatic hydrocarbons in the liquid product there occurs also a substantial production of unsaturated aliphatic hydrocarbons. For example, in the conversion of heptane to toluene under conditions effective to produce an appreciable proportion of toluene in the liquid product the latter also contains a substantial proportion of heptene. The proportion of toluene in the liquid product is quite responsive to variations in the operating conditions so that wide variation in the proportion of toluene in the liquid product may be effected by suitable variation of the operating conditions. The proportion of heptene in the liquid product is, however, much less responsive to variations in the operating conditions, and it is found that if the conditions are controlled to produce an appreciable proportion of toluene in the liquid product the proportion of heptene in the liquid product will remain fairly constant, varying only between limits of approximately 10 to 17 per cent by volume.

We have discovered that the catalytic properties of chromium oxide such as the gel-type material described above can be modified by the incorporation therein of a substantial proportion of zinc oxide whereby the modified catalyst is effective to promote a substantial conversion of aliphatic paraffinic hydrocarbons to aromatic hydrocarbons while producing olefinic aliphatic hydrocarbons to a substantially lesser degree.

The modified catalyst employed in the present invention is prepared preferably by effecting the co-precipitation of chromium oxide and zinc oxide under conditions wherein a gelatinous precipitate is formed. The gelatinous precipitate is then converted to the catalytic form by the methods of preparation customarily employed in the production of gel-type chromium oxide catalysts. It is to be understood, however, that the zinc oxide may be incorporated in the modified catalyst by any means which effect the production of catalysts having the desired properties with reference to the production of olefinic aliphatic hydrocarbons. The invention will be described further by reference to specific examples of the preparation and testing of chromium oxide-zinc oxide catalysts. It is to be understood, however, that the invention is not to be limited to the use of a catalyst prepared in

accordance with the specific methods of preparation outlined below nor to the treatment of the hydrocarbons referred to under the specific operating conditions employed.

A highly active chromium oxide gel-type catalyst may be prepared by slow precipitation of the gel in a dilute aqueous solution of a chromium salt. For example, the gel may be prepared by the slow addition of 0.1 normal ammonium hydroxide to 6 litres of a 0.1 solution of chromium nitrate. The ammonium hydroxide is added dropwise to the chromium nitrate solution and with vigorous stirring. The addition of the first half of the ammonium hydroxide necessary to effect precipitation to the chromium nitrate solution is carried out slowly at the rate of about 0.5 liter per hour. After the addition of approximately half the ammonium hydroxide the solution is stirred long enough to dissolve any temporary precipitate which may have formed. The remainder of the hydroxide is then added with continuous stirring. On completion of the addition of ammonium hydroxide the precipitate is allowed to settle, and the excess liquid removed by decantation. The precipitate is then washed several times by agitation with fresh water, followed by settling and decantation of the water. Washing is continued to the point of incipient peptization of the chromium oxide. The precipitate is then filtered and dried, for example at 100° C., for several hours to convert it to a black, relatively dense granular form. Prior to use this material should be heated gradually to approximately 300° C. and held at that temperature for about 10 hours in order to stabilize it against physical disintegration on its being rapidly heated to the reaction temperature.

The modified catalyst employed in the present invention is prepared preferably by a modification of the foregoing procedure for the preparation of a gel-type chromium oxide catalyst. In accordance with this modification a suitable zinc compound, for example, zinc nitrate is added to the chromium nitrate solution. For example, a solution which is one-tenth normal in the chromium nitrate and one-tenth normal in zinc nitrate may be employed, and a 0.166 normal solution of ammonium hydroxide may be employed to effect the formation of a gelatinous precipitate. In this manner a precipitate containing chromium oxide and zinc oxide in approximately equal molecular proportions is obtained.

The zinc oxide should be incorporated in the catalyst in a proportion sufficient to effect the desired modification of the catalytic properties of the chromium oxide catalyst but not sufficiently great to change the essential character of the chromium oxide as a cyclicizing catalyst. The modified procedure for the preparation of the catalyst as outlined above produces a catalyst containing approximately equal molecular proportions of chromium oxide and zinc oxide. This ratio is satisfactory but is, however, an example which may be departed from by employing other suitable proportions.

While the catalytic material employed in the present invention may consist of a mixture of chromium oxide and zinc oxide, suitable supporting materials may be employed in addition to the essential constituents. For example, a mixture of chromium oxide and zinc oxide may be precipitated on a suitable supporting material such as activated alumina, or the gelatinous mixture of these oxides may suitably be incorporated with supporting material after precipitation and prior to drying.

A gel-type chromium oxide catalyst and a gel-type chromium oxide-zinc oxide catalyst prepared in accordance with the methods described above were tested for catalytic activity in the conversion of normal heptane to toluene. Comparative data based on these tests are set forth in the following table.

Catalyst	Analysis of liquid product		Ratio of aromatics to olefins in liquid product
	Weight percent aromatics	Weight percent olefins	
Chromium oxide	8.9	15.8	0.56
Chromium oxide-zinc oxide	8.9	4.9	1.81

The data given in the foregoing table are based on operations at 475° C. and atmospheric pressure at space velocities of 1.5 to 1.7 liquid volumes of heptane per volume of catalyst space per hour in operating runs of substantially the same length.

The data set forth in the table demonstrate that the chromium oxide-zinc oxide catalyst is capable of converting heptane to liquid containing a substantial proportion of toluene and a proportion of heptene which is substantially less than that obtained under the same conditions in connection with the use of chromium oxide catalysts containing no zinc oxide. The data demonstrate that by employing the catalyst of the present invention heptane may be converted to a liquid product containing a substantial proportion of aromatic hydrocarbons while effecting the formation in the liquid product of olefinic hydrocarbons in an amount about one-third that produced by the chromium oxide catalyst in producing a liquid product having the same content of aromatic hydrocarbons.

While the invention has been illustrated by reference to the treatment of a single hydrocarbon compound the process is equally applicable to the treatment of mixtures of hydrocarbons. For example, the process can be applied to the dehydrogenation treatment of a gasoline of low anti-knock value to improve its anti-knock qualities. For example, a paraffinic naphtha may be treated to improve its anti-knock value by increasing the proportion of aromatic hydrocarbons therein while at the same time restricting the formation of olefinic hydrocarbons in the product. This permits the production of a gasoline which is relatively more stable and is particularly advantageous in meeting acid heat specifications for aviation gasoline, which require that the percentage of polymerizable materials contained in the gasoline shall be substantially restricted. The new process is advantageous also in the production of aromatic hydrocarbons where extraction of the aromatic hydrocarbons from the liquid product is complicated by the presence of substantial amounts of olefinic hydrocarbons.

We claim:

1. A process for the conversion of aliphatic hydrocarbons having at least 6 carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons with a catalyst essentially consisting of a mixture of substantial proportions of chromium oxide and zinc oxide, and maintaining contact of said hy-

drocarbons with said catalyst at a temperature sufficiently high and at a flow rate per unit of catalyst volume sufficiently low to effect conversion of said hydrocarbons to a liquid product containing a substantial proportion of aromatic hydrocarbons.

2. A process for the conversion of aliphatic hydrocarbons having at least 6 carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons with a gel type catalyst essentially consisting of a mixture of substantial proportions of chromium oxide and zinc oxide at a temperature sufficiently high and at a flow rate per unit of catalyst volume sufficiently low to effect conversion of said hydrocarbons to a liquid product containing a substantial proportion of aromatic hydrocarbons.

3. A process for the conversion of aliphatic hydrocarbons having at least 6 carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons with a catalyst essentially consisting of a mixture of chromium oxide and zinc oxide prepared by coprecipitation of chromium oxide and zinc oxide in aqueous solution under conditions effective to produce a gelatinous precipitate, and maintaining said hydrocarbons in contact with said catalyst at a temperature sufficiently high and at a flow rate per unit of catalyst volume sufficiently low to effect conversion of said aliphatic hydrocarbons to aromatic hydrocarbons.

4. A process for the conversion of aliphatic paraffinic hydrocarbons having at least six carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof, which comprises contacting said aliphatic paraffinic hydrocarbons with a chromium oxide catalyst containing zinc oxide in intimate mixture therewith whereby the catalytic properties of the chromium oxide are modified by zinc oxide, said contact of said hydrocarbons with said catalyst being effected at a temperature of 450 to 550° C. and at a space velocity of less than two volumes of hydrocarbons (liquid basis) per volume of catalyst space per hour.

5. A process for the conversion of aliphatic hydrocarbons having at least six carbons per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons with a chromium oxide catalyst containing zinc oxide in intimate mixture therewith whereby the catalytic properties of the chromium oxide are modified by the zinc oxide, said contact of said hydrocarbons with said catalyst being effected at a temperature above 400° C. and at a space velocity of less than two volumes of hydrocarbons (liquid basis) per volume of catalyst space per hour.

6. A process for the conversion of aliphatic hydrocarbons having at least six carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons with a chromium oxide catalyst containing zinc oxide in admixture therewith in a molecular ratio of 1:1, said contact of said hydrocarbons with said catalyst being effected at a temperature above 400° C. and at a space velocity of less than two volumes of hydrocarbons (liquid basis) per volume of catalyst space per hour.

7. A process for the conversion of aliphatic hydrocarbons having at least six carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons with a gel type chromium oxide catalyst containing zinc oxide in intimate mixture therewith whereby the catalytic properties of said chromium oxide are modified by the zinc oxide, said contact of said hydrocarbons with said catalyst being effected at a temperature above 400° C. and at a space velocity of less than two volumes of hydrocarbons (liquid basis) per volume of catalyst space per hour.

8. A process for the conversion of aliphatic hydrocarbons having at least six carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons with a catalyst comprising an intimate mixture of chromium oxide and zinc oxide prepared by coprecipitation of chromium oxide and zinc oxide in aqueous solution under conditions effective to produce a gelatinous precipitate, said contact of said hydrocarbons with said catalyst being effected at a temperature above 400° C. and at a space velocity of less than two volumes of hydrocarbons (liquid basis) per volume of catalyst space per hour.

9. A process for treating a paraffinic naphtha to produce a gasoline of improved anti-knock value and low acid heat which comprises contacting said paraffinic naphtha with a chromium oxide catalyst containing zinc oxide in intimate mixture therewith whereby the catalyst properties of the chromium oxide are modified by the zinc oxide, said contact of said naphtha with said catalyst being effected at a temperature above 400° C. and at a space velocity of less than two volumes of naphtha (liquid basis) per volume of catalyst space per hour.

10. A process for treating a paraffinic naphtha to produce a gasoline of improved anti-knock value and low acid heat which comprises contacting said paraffinic naphtha with a gel-type chromium oxide catalyst containing zinc oxide in intimate mixture therewith whereby the catalyst properties of the chromium oxide are modified by the zinc oxide, said contact of said naphtha with said catalyst being effected at a temperature above 400° C. and at a space velocity of less than two volumes of naphtha (liquid basis) per volume of catalyst space per hour.

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