Patented Jan. 5, 1943

2,307,715

UNITED STATES PATENT OFFICE

2,307,715

HYDROCARBON CONVERSION

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No Drawing. Application August 29, 1940, Serial No. 354,697

5 Claims. (Cl. 260—668)

This invention relates to the catalytic dehydrogenation of hydrocarbons. More particularly, the invention relates to the dehydrogenation of hydrocarbons by contact thereof with a catalyst prepared by the reduction of chromium sulfate.

I have discovered that a highly active catalytic material for the dehydrogenation of hydrocarbons, and particularly for the conversion of aliphatic hydrocarbons of six or more carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization reactions, may be prepared by the reduction of chromic sulfate. Preferably, such reduction is carried out by the passage of hydrogen over the chromic sulfate while raising the temperature thereof slowly to the reaction temperature.

The exact chemical composition of the reduced material is not certain, but the material apparently consists of a mixture of chromic sulfide and chromic oxide. This mixture exhibits substantially greater activity in the dehydrogenation of hydrocarbons, and particularly in the formation of aromatic hydrocarbons, than an equal quantity of a highly active gel-type chromium oxide catalyst.

In the preparation of the catalyst the chromic sulfate which may be either the violet variety ($Cr(SO_4)_3.18H_2O$) or the green variety

($Cr(SO_4)_3.15H_2O$)

is heated relatively slowly to the reaction temperature in a stream of hydrogen or other suitable reducing atmosphere. Preferably, the sulfate is heated to a final temperature of approximately 450° to 550° C.

Example

Chromic sulfate was heated to a temperature of 475° C. in an atmosphere of hydrogen during a period of approximately 12 hours. During this time free sulfur was distilled, and the resulting material apparently was a mixture of chromic sulfide and chromic oxide. The material thus produced was employed in the dehydrogenation treatment of normal heptane at 472° C. and atmospheric pressure. The heptane was passed over the catalyst in the vapor phase at a space velocity of approximately 2 volumes of heptane (liquid basis) per volume of catalyst space per hour. During the course of a two-hour operating run gas, consisting essentially of hydrogen, was produced at the rate of approximately 230 volumes per liquid volume of heptane charge. The liquid product recovered in this time contained 13 per cent aromatic hydrocarbons (toluene) and 9 per cent olefinic hydrocarbons (heptene). The liquid product produced by this operation contained over twice the proportion of aromatic hydrocarbons contained in the liquid product of a similar operation employing a gel-type chromium oxide catalyst.

The process of the invention as illustrated by the foregoing example is particularly applicable to the conversion of aliphatic hydrocarbons containing at least six carbon atoms per molecule to aromatic hydrocarbons. In the conversion of aliphatic hydrocarbons to aromatic hydrocarbons by means of the present process the hydrocarbon vapors are passed over the catalyst at a temperature in the range of 325° to 650° C., preferably 450° to 550° C. at atmospheric or higher pressure. The hydrocarbons are passed over the catalyst at a space velocity which, while sufficient to effect production of aromatic hydrocarbons at a substantial rate, is 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. At lower temperatures within the above-mentioned temperature range a lower space velocity may be employed while at higher temperatures a higher space velocity may be used. In general the space velocities which may be employed advantageously for the production of aromatic hydrocarbons fall within the range of 0.1 to 3 volumes of aliphatic hydrocarbons (liquid basis) per volume of catalyst space per hour. Preferably, space velocities within the range of 1 to 2 volumes of liquid per volume of catalyst per hour are employed.

While the invention is particularly adapted to the conversion of aliphatic hydrocarbons to aromatic hydrocarbons by dehydrogenation and cyclization reactions, the process is applicable also to the dehydrogenation of other hydrocarbons such as normally gaseous hydrocarbons to form corresponding unsaturated hydrocarbons.

While the invention has been illustrated by reference to a single hydrocarbon compound, the process is equally applicable to the treatment of mixtures of hydrocarbons. For example, the process may be applied to the dehydrogenation treatment of a gasoline of low anti-knock value to improve its anti-knock qualities by the conversion of aliphatic hydrocarbons contained therein to aromatic hydrocarbons and by the production therein of other unsaturated constituents.

The improved catalytic material may be used

as such in the dehydrogenation treatment, or may be employed in association with other active or inactive materials. For example, the chromic sulfate may be deposited on a suitable supporting material, such as alumina, prior to reduction in the manner described above, to produce a compound catalyst.

I claim:

1. The method of dehydrogenating hydrocarbons which comprises contacting said hydrocarbons at elevated temperature with a catalyst essentially comprising an intimate mixture of chromic sulphide and chromic oxide, said mixture having been prepared by heating chromic sulfate in a reducing atmosphere to effect reduction of the sulfate to a mixture of the sulphide and oxide.

2. The method of dehydrogenating hydrocarbons which comprises contacting said hydrocarbons at elevated temperature with a catalyst prepared by heating chromic sulfate in an atmosphere of hydrogen to the dehydrogenation reaction temperature to effect substantial reduction of the chromic sulfate to chromic oxide.

3. The method of dehydrogenating hydrocarbons which comprises contacting said hydrocarbons at elevated temperature with a catalyst prepared by heating a hydrated chromic sulfate in an atmosphere of hydrogen to a temperature within the range of 450° to 550° C. to effect substantial reduction of the chromic sulfate to chromic oxide.

4. The method of converting aliphatic hydrocarbons containing at least six carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons at elevated temperature with a catalyst essentially comprising an intimate mixture of chromic sulphide and chromic oxide, said mixture having been prepared by heating chromic sulfate in a reducing atmosphere to effect reduction of the sulfate to a mixture of the sulphide and oxide.

5. The method of converting aliphatic hydrocarbons containing at least six carbon atoms per molecule to aromatic hydrocarbons by dehydrogenation and cyclization thereof which comprises contacting said aliphatic hydrocarbons at elevated temperature with a catalyst prepared by heating a hydrated chromic sulfate in an atmosphere of hydrogen to a temperature of 450° to 550° C. to effect substantial reduction of said sulfate and substantial removal of sulfur therefrom to form a catalyst material comprising an intimate mixture of chromic oxide ond chromic sulphide.

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