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PROCESS FOR AROMATIZING AND DEHYDROGENATING HYDROCARBONS

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In the known processes for producing aromatic hydrocarbons from hydrocarbons with a higher hydrogen content, it is necessary to make a fundamental distinction between removing hydrogen from saturated ring systems (naphthenes) and forming a ring from straight-chain hydrocarbons, more especially from paraffinic hydrocarbons. Naphthenic hydrocarbons admit of comparatively ready conversion into aromatic compounds by the use of simple catalysts. In the known increase in knock rating of liquid fuels the problem should almost exclusively be one of converting saturated ring systems into aromatic ring systems.

For this purpose catalysts have already been proposed that consist of chromium precipitated upon a suitable carrier substance such as active carbon. It has already been proposed to employ, in the treatment of Pennsylvania benzines, mixed chromium catalysts that have been precipitated on magnesite.

Further, catalysts are known that are capable of forming aromatic substances from paraffinic hydrocarbons such as hexane or heptane, the catalysts being prepared with suitable carrier substances such as pumice stone, bleaching clays, Bentonite, magnesite, active carbon and the like and do not contain more than 10% of the active metal for example chromium. A particularly suitable proportion of chromium is given as being from 1 to 2%.

In addition to these chromium catalysts precipitated on carrier substances, contact substances are known for the same purpose that consist exclusively of chromium oxide.

It has been found that all these known aromatizing and dehydrogenating catalysts are suitable in the use of particular hydrocarbons only. It is not possible to produce—or at any rate only a very small quantity—aromatic hydrocarbons from a mixture of straight-chain paraffinic and olefinic hydrocarbons by their use. Such a conversion however has great practical importance, because for example in the synthesis of hydrocarbons from carbon-monoxide and hydrogen, large quantities of such hydrocarbon mixtures are produced. In contradistinction to naturally recovered hydrocarbons, synthetic products contain practically no naphthenes.

For this reason it has not been possible to transfer either the experience secured in aromatizing natural hydrocarbons or the knowledge obtained in the dehydrogenation of pure aliphatic substances such as normal hexane or normal heptane, to the aromatizing of synthetic hydrocarbon mixtures. Experiments have shown that the

chromium catalysts heretofore described fail in the aromatization of synthetic hydrocarbons.

If for example a catalyst that has been produced for the dehydrogenation of normal hexane by the decomposition of chromium nitrate on pumice stone, be used, it is possible by its use to convert normal heptane to about 80%, into toluol at a temperature of from 460 to 480° C. When a heptane containing 10% of normal heptane be used the catalyst fails completely because polymers are formed that render the contact surface useless in a very short time.

When isomeric octanes that boil within a range of about 5° C are treated, the chromium catalyst also becomes inactive within a few minutes. Furthermore chromium catalysts precipitated on other carrier substances such as active carbon, are not suitable for the treatment of hydrocarbon mixtures.

It has now been found that a catalyst consisting of calcined magnesite as carrier and chromium oxide as activator is particularly suitable for aromatizing and dehydrogenating mixtures, under practical conditions, of aliphatic hydrocarbons of a wide boiling range when the content of chromium oxide is above 10% and advantageously between 30 and 50%.

Chromium oxide can be applied to the carrier substance in various known ways. Magnesite is advantageously impregnated a number of times with a solution of ammonium chromate, whereupon the ammonia is driven off by heat treatment, advantageously in the presence of reducing gases, so that chromium oxide is left behind.

An aqueous solution of chromic acid may be treated instead of solutions of ammonium chromate. In such case the catalyst is reduced with hydrogen or gases containing hydrogen at elevated temperature, for example at temperatures that are subsequently used for aromatization or dehydrogenation. Gases from which hydrogen breaks off such as hydrocarbon gases may be employed for reducing purposes.

Other solutions of chromium salts for example solutions of an organic character may be used for impregnating the magnesite; but solutions of chromium nitrate have not proved advantageous.

Besides chromium oxide, there may be added suitable promoters such as (compounds of Mn, Ni or Co and Th). In this way the catalytic activity of the chromium and magnesite contact substances used can be very considerably increased.

The following Example described a usable method of producing the catalyst employed.

Example 1.—1,000 gm of natural magnesite were calcined at 850°C. The carrier substance thus obtained was evacuated and thereupon impregnated with a solution of ammonium chromate saturated while cold. At the same time the magnesite was heated. After cooling the material was carefully dried, evacuated, and again impregnated with a solution of ammonium chromate. This treatment was repeated again and again until 1,000 gm of magnesite had absorbed about 400 gm of chromium oxide (Cr_2O_3). This mixture was dried at about 450°C. in a vacuum and allowed to cool in vacuum. Thereupon the conversion furnace was charged with the catalyst which was heated to the reaction temperature of about 480°C. within from 4 to 5 hours while a little hydrogen was passed through. The catalyst was then ready for use.

A conversion contact substance produced in this way has good dehydrogenating and aromatizing qualities.

At first this catalyst is particularly suitable for dehydrogenation, carried out without ring formation, of short chain paraffin hydrocarbons such as propane and butane as described in the following Example.

Example 2.—Propane was passed at a temperature of 480°C, over a catalyst consisting of 35% chromium oxide and 65% calcined magnesite at a velocity of 25 litres of gas per hour, per 1 litre of contact substance. The gas issuing from the reaction furnace contained about 15 to 20% propylene.

Such dehydrogenation of short chain paraffin hydrocarbons is generally carried out under atmospheric pressure. If the reaction be carried out under a partial vacuum, there is an increase in the yield of unsaturated hydrocarbons. The partial vacuum may be produced in the form of a reduced partial pressure by the admixture of inert gases (such as hydrogen or nitrogen) that do not take part in the reaction.

The catalyst produced, as described in Example 1, converts not only purely saturated aliphatic substances (such as normal hexane, normal heptane, normal octane or normal nonane) into aromatic substances with corresponding side chains such as benzene, toluol, xylol and the like; the catalyst is furthermore almost completely insensitive to the presence of olefines or isomeric aliphatic substances. Hence fractions of wide boiling range can be treated, for example all the benzines, boiling at between 60 and 150°C, derived from the hydrogenation of carbon monoxide.

The products obtained are light in colour like water and of a pleasant smell characteristic of the pure aromatic hydrocarbons.

Example 3.—Pure normal heptane was passed at a temperature of 460 to 480°C over a catalyst that consisted of 35% chromium oxide and 65% calcined magnesite. The product was toluol, that corresponded to an 80% conversion of the normal heptane used.

When aromatizing aliphatic hydrocarbons by the use of catalysts of chromium oxide and magnesite, there is produced a certain quantity of hydrocarbons in the form of normal gas in addition to the aromatic substances. Furthermore there are produced carbonaceous separations that render the surface of the catalyst inactive.

It has been found that these undesirable side reactions decrease or can be entirely avoided by mixing short chain aliphatic hydrocarbons with the aromatizing hydrocarbon mixtures. These aliphatic hydrocarbons may be either saturated or unsaturated, and may consist for example of hydrocarbon gases with from 2 to 4 carbon atoms. The addition of olefinic hydrocarbons produces a higher yield of aromatic substances.

As the Examples that follow show, the formation of cracked gases can be lowered to such an extent that practically only additional hydrogen is produced. The ratio of the aromatic substances to the reaction gas produced corresponds, when normal heptane for example is treated, to the theoretic equation

$$C_7H_{16}=C_6H_5.CH_3+4H_2$$
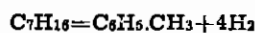
The small excess of hydrogen is due to the formation of carbonaceous decomposition products.

Example 4.—Heptane was conducted at a velocity of 20 gm per hour at 480°C. over 300 cc of a catalyst of magnesite and chromium oxide, with about 25% by weight of chromium oxide. The final liquid product was a colourless mixture of heptane, heptene and toluol. The toluol content amounted to 44% by volume. From 100 gm. heptane there were obtained 82 gm. liquid products with 41 gm. toluol and 15 gm. gas or 3 gm. coke separations. The amount of gas produced was about 11% of the aromatic substances formed (ratio by weight).

Example 5.—Heptane was passed at a throughput velocity of 20 gm. per hour at 480° C. over 300 cc. of the catalyst referred to in Example 4. At the same time nitrogen moving at a velocity of 4000 cc. per hour was added. The resulting final product contained 40% by volume of toluol. From 100 gm. heptane there were produced 84 gm. liquid products, with 38 gm. toluol, also 13 gm gas and 3 gm carbonaceous products of decomposition. The gas produced amounted to about 30% of the aromatic substances formed (ratio by weight).

Example 6.—Heptane was passed at a throughput velocity of 20 gm per hour at 480° C. over 300 cc of the contact substance used in Example 4, and 4000 cc of propane were added per hour. The liquid products contained 42% by volume of toluol. From 100 gm heptane there were produced 91 gm liquid products, with 50 gm toluol, also 5 gm gas, and 4 gm decomposition products resembling coke. The gas produced amounted to about 10% of the aromatic substances formed (ratio by weight).

Example 7.—Heptane was passed at a throughput velocity of 20 gm. per hour over 300 cc. of the catalyst used in Example 4, and 4000 cc. of ethylene were also added per hour. The liquid products contained 63% by volume of toluol. From 100 gm. heptane there were obtained 90 gm. liquid products, with 62 gm. toluol, also 6 gm. gas and 4 gm. carbonaceous decomposition products. The gas produced amounted to about 10% of the aromatic substances obtained (ratio by weight).

Example 8.—20 gm. of a benzine fraction boiling between 96 and 160° C. were passed hourly over 300 cc of the catalyst used in Example 4, the benzine having first been separated from the products of the hydrogenation of carbon monoxide by the use of active carbon. The reaction temperature was maintained at about 460 to 480° C. The end products were 87% by weight of normally liquid hydrocarbons with 40% by volume of aromatic substances. There were at the same time produced 6.8% by weight of cracked gases and 3% by weight of coke separations.

The catalysts that were used according to the invention can be regenerated in a particularly easy way. To effect regeneration the hydrocar-

bon gases present in the contact substance are in the first place displaced by nitrogen. Thereupon air is passed over the catalyst at the conversion temperature employed, that is to say at about 480° C. After the displacement of the air by nitrogen the contact substance is treated for a further short period with hydrogen.

Such catalysts are effective for months with unvarying yield and at an unchanging conversion speed. It is an important fact that the catalysts differ from the conversion contact substances hitherto employed in that they contain a large quantity of chromium oxide, that is to say far above 10% and advantageously 30 to 50%.

Conversion can be effected both under ordinary pressure and under a slight superpressure or under a partial vacuum. The reaction is advantageously continued only until the hydrogen content of the final gas from which the liquid reaction products have been removed by condensation, amounts to at least 80%. Thereupon the catalyst is regenerated by combustion with air until the CO_2 content of the combustion gases has dropped to about from 1 to 5%. Thereupon the regenerated catalyst is further treated with hydrogen.

The catalysts according to the invention are very active not only in the treatment of the hydrocarbons obtained by the hydrogenation of carbon monoxide, but also for the conversion of the products of hydrogenation under high-pressure or in the conversion of natural hydrocarbon mixtures. If products of the hydrogenation of carbon monoxide are treated by means of the process hereinbefore described, it is advantageous to make use of the fractions that boil up to about 200° C, these fractions consisting wholly or for the major part of saturated hydrocarbons.

Conversion can be carried out in the usual apparatus employed for the purpose, which is used for example from 60 to 90 minutes for aromatizing and regeneration of the catalyst is then effected by calcination.

The objection arises that the catalysts prepared according to the invention incline to form powder. If the catalyst be employed in deep vertical layers the reaction is disturbed by this formation of powder. It has been found that these disadvantages do not arise if the catalysts referred to are used in less deep horizontal layers or slightly inclined layers. Advantageously reaction tubes disposed parallel are employed for the purpose, the tubes being heated within a common chamber with circulating flue gas. The temperature required for carrying out the conversion can be produced by heat derived from burners.

If carbon deposited on the catalyst be calcined, unalloyed iron tubes and the majority of alloyed iron tubes have imparted to them an injurious activity whereby the separation of carbon is facilitated. This objection thus leads to an increased formation of loose carbon on the walls of the tubes and affects the smooth course of the conversion. It has been found that these disadvantages do not occur if the conversion be carried out in reaction chambers that are made of a material that remains inactive even when air is blown through repeatedly. The most suitable reaction tubes are those made from a ceramic substance or metal tubes that consist of alloys having a considerable content of silicon or aluminium.

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