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## PROCESS FOR THE SELECTIVE HYDROGENATION OF BUTADIENE-(1,3) IN A HYDROCARBON MIXTURE CONTAINING IT AND A LARGER QUANTITY OF BUTENE-(1)

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3 Claims

### ABSTRACT OF THE DISCLOSURE

Butadiene-(1,3), present in very small amount in a hydrocarbon mixture containing a much larger quantity of butene-(1), is selectively hydrogenated by reacting with hydrogen in the presence of a copper-nickel-containing carrier catalyst composition in which the metal content varies between 2 and 60 percent by weight of the composition and in the metal content the ratio of copper to nickel varies from 10:1 to 1:1.

In the workingup of products, obtained by the pyrolysis of crude oil, fractions are produced that consist principally of C<sub>4</sub>-hydrocarbons such as n-butane, n-butene-1, cis-butene-2, transbutene-2 and butadiene-(1,3). Further fractionation will result in fractions consisting principally of butenes, butane and small quantities of butadiene. Further separation of the butadiene by fractionation is unrewarding but its presence interferes with the general use of these products.

In order to remove the butadiene from such mixtures which contain mainly n-butene-1, cis- and trans-butene-2 and n-butane, relatively inexpensive selective hydrogenation is employed. For example hydrogenation by means of sulfidic cobalt-molybdenum-carrier catalysts (French Patent No. 1,253,588), copper chromite catalysts (U.S. Patent No. 2,964,579) and copper catalysts which contain .1 to .001% of Pd, Ru, Fe, Ni, Rh, Ir or Pt (U.S. Patent No. 3,076,858) have been employed. For the liquid phase hydrogenation Pd-carrier catalysts are employed (Erdoel und Kohle, Erdgas, Petrochemie 16, pages 522 to 523—1963).

In many instances it is desirable to preserve or to increase the butene-1 content if for the purpose of subsequent reactions, such as polymerizations, only the butene-1 is to be used.

For a fully selective hydrogenation of the butadiene to butenes without formation of butane there is also required a fully selective hydrogenation to butene-1 without isomerization of the butene-1 to butene-2. This requirement is difficult to fulfill in case of high butene-1 contents due to the thermodynamic equilibrium which lies predominantly on the butene-2 side since the equilibrium establishment is accelerated not only thermally but also generally by the hydrogenation catalysts. The methods known heretofore could not, or only unsatisfactorily, satisfy these requirements.

A method has now been found for the selective hydrogenation of butadiene-(1,3) in a hydrocarbon mixture containing larger quantities of butene-(1) as well as lesser quantities of butadiene-(1,3) by the use of a copper-nickel carrier catalyst having a metal content within the

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range from 2 to 60 percent by weight and the copper-nickel ratio within the ranges from 10:1 to 1:1.

The catalyst can contain the known modifiers for copper catalysts such as chromium, chromium oxide, phosphate or magnesium. The modifiers are employed in quantities of from .05 to 15 percent by weight, preferably .2 to 3 percent by weight, relative to the total weight of the catalyst.

The butadiene containing C<sub>4</sub>-hydrocarbon mixtures employed, comprising for example butene-1, cis- and trans-butene-2, n-butane, isobutene and isobutane, have a content of butadiene-1,3 of up to approximately 5 mol-percent and small quantities of other hydrocarbons, for example C<sub>3</sub>- and C<sub>5</sub>-hydrocarbons, can also be present. If small quantities of acetylenes such as ethyl- or vinylacetylene, or compounds with cumulated double bonds such as propadiene or butadiene-1,2 are present, they will be hydrogenated together with the butadiene-1,3.

In order to carry out the hydrogenation, hydrogen must be added to the mixture unless it is already present. The quantity of hydrogen required depends on the content of butadiene-1,3 or the compounds to be hydrogenated and must be at least equimolecular to them but can also be a multiple thereof, for example five or tenfold molarwise. Molar ratios between approximately 1.2 and 3 are advantageous.

The method permits the employment of hydrogen at such a specific quantity that for all practical purposes no hydrogen will be left in the hydrogenated hydrocarbon mixture which is an important feature in case of further processing, for example by polymerization, because small quantities of hydrogen will often interfere with the reaction.

The hydrogenation temperature should range from 40 to 200° C., and preferably between 70 and 130° C. It is advisable to set the temperature as low as feasible, depending on the quantity of the hydrogen and the quantity of throughput. A high hydrogen content and a low throughput will permit the use of a lower temperature.

The throughput quantity normally ranges from 2 to 12 kg. of hydrocarbon mixture per hour and per liter of catalyst at butadiene contents between approximately 4 and .4 mol-percent. A higher content of butadiene will lower the maximum throughput value but there is no need to maintain any specific throughput value.

The process can be carried out either under normal pressure or lower as well as higher pressure, ranging preferably from .2 to 30 atmospheres absolute pressure. If the C<sub>4</sub>-hydrocarbon mixture is not to be further processed in the gaseous state, it is advantageous to operate at hydrogenation pressures of 4 to 8 atmospheres so that the mixture will be in the liquid state at room temperature.

The mixed catalysts are prepared by the simultaneous impregnation of a carrier with solution or suspension of a copper salt such as copper carbonate, copper acetate, copper formate or copper nitrate and a nickel salt such as nickel carbonate, nickel acetate, nickel formate or nickel nitrate, optionally with an addition of ammonia to improve solubilization. Also, if desired, chromic acid, phosphates or magnesium salts which are standard modifiers for copper catalysts can be added. It is also possible to fix these salts to the carrier by means of auxiliary materials such as sodium silicate. The solutions or suspensions are prepared and applied to the carrier in such manner that the copper/nickel ratio of the completely reduced carrier-catalyst will range from 10:1 to 1:1, and preferably from 5:1 to 2:1. It is expedient to desiccate the

catalyst and it can be subjected to an intermediate thermal treatment at approximately 300 to 400° C. It is advisable to reduce the catalyst, in a manner known per se, by the use of hydrogen at approximately 100 to 250° C. prior to the addition of the mixture to be hydrogenated.

Suitable carrier materials are for example silica gel, pumice, kaolin, aluminum oxide and magnesium oxide. The carrier material content of the total catalyzer ranges from 40 to 98 percent by weight, and corresponding thereto the content of the activating metals ranges from 2 to 60 percent by weight.

These catalysts are very durable and will retain, under normal operating conditions, their activity and selectivity for long periods of time, and at least for several months. If their activity lessens they can be regenerated in the usual manner by treatment with air at 200 to 400° C. and reactivated by subsequent treatment at approximately 100 to 250° C. with hydrogen.

To summarize the method of the present invention offers the advantage of very high selectivity for the hydrogenation of the butadiene-1,3 to butene-1 without any substantial isomerization to butene-2 and without the formation of significant quantities of butadiene. Also, the activity and selectivity of the catalyst will last for a long period of time.

Therefore, this method is particularly suitable if it is desired to obtain butene-1 for further processing. Also advantageous is the possibility to obtain a product which for practical purposes contains no hydrogen. Compared with methods employing sulphidic catalysts it offers the advantage that the hydrogenation product does not contain any sulphur compounds which will often interfere with further processing. However, small quantities of sulphur, for example 20 p.p.m., which might be present in the original mixture, will be tolerated by the catalyst of the present invention. Compared with copper chromite catalysts the invention has the advantage of greater selectivity, and in case of activated copper catalysts the additional advantage of lower hydrogenation temperatures which in turn has a favorable effect on the suppression of the isomerization to butene-2 and on the durability of catalyst.

Compared with the hydrogenation in the liquid phase with palladium catalysts the method of the present invention again provides much better selectivity if utilization of the butene-1 is desired as is proved by the literature (see i.e. "Erdoel und Kohle") because the butadiene hydrogenated by use of the liquid phase method is obtained in the form of n-butene-2 and a certain isomerization from n-butene-1 to n-butene-2 will take place also.

#### Example 1

The starting material was a C<sub>4</sub>-fraction of the following compositions:

	Mol percent
i-Butane -----	1.0
n-Butane -----	4.2
i-Butene -----	.4
n-Butene-1 -----	79.2
Trans-butene-2 -----	8.8
Cis-butene-2 -----	4.8
Butadiene-1,3 -----	1.5
C <sub>5</sub> -hydrocarbons -----	.1

Prior to entering the hydrogenation furnace the fraction is mixed with 2.0 percent by volume of hydrogen and is then conducted in the gaseous state at a volume space velocity of 1500 NL/h. at atmospheric pressure over 1 liter of catalyst. The hydrogenation furnace has a temperature of 100 to 110° C. The catalyst was prepared by simultaneous application of basic copper carbonate, nickel carbonate and magnesium carbonate onto pumice with the aid of sodium silicate so that the content of copper was 10.5%, the content of nickel 2.5% and the content of magnesium 1.1%. Prior to its use the catalyst was reduced by means of hydrogen at 200° C.

The hydrocarbon mixture leaving the hydrogenation furnace had the following composition (disregarding the slight quantity of hydrogen):

	Mol percent
i-Butane -----	1.0
n-Butane -----	4.2
i-Butene -----	.4
n-Butene-1 -----	80.8
Trans-butene-2 -----	8.7
Cis-butene-2 -----	4.8
Butadiene-1,3 -----	1.5
C <sub>5</sub> -hydrocarbons -----	.1

For all practical purposes the butadiene was eliminated (<.005%) and selectively hydrogenated to butene-1 without additional production of butane and without any isomerization from butene-1 to butene-2.

After 200 days of operation there were hardly any change in the activity and selectivity of the catalyst but the hydrogenation temperature was raised slightly from 110 to 120° C.

#### Example 2

A hydrocarbon mixture containing

	Mol percent
n-Butane -----	4.8
n-Butene-1 -----	62.1
Trans-butene-2- -----	18.7
Cis-butene-2- -----	11.5
Butadiene-1,3 -----	1.3

and approximately 1.6 mol-percent of iso-butane, iso-butene, and C<sub>3</sub>- and C<sub>5</sub>-hydrocarbons was conducted, after admixture of 1.8 mol-percent of hydrogen, at a pressure of 5 atmospheres gauge pressure, at the rate of 8 kg. per hour and at a hydrogenation temperature of 90 to 100° C. over 1 liter of a catalyst which contained 10% of Cu, 2% of Ni and .5% of Cr on silica gel. The catalyst was prepared by impregnating the silica gel with the aqueous solution of the proper quantities of copper and nickel nitrates and chromic acid, roasting at 300 to 350° C. and reduction with hydrogen at approximately 200° C. The hydrocarbon mixture, upon leaving the hydrogenation furnace, had the following contents (disregarding the small quantity of hydrogen):

	Mol percent
n-Butane -----	4.8
n-Butene-1 -----	63.6
Trans-butene-2- -----	18.6
Cis-butene-2- -----	11.4

with the remainder being other hydrocarbons. The butadiene-1,3 was reduced to less than .005 mol-percent.

#### Example 3

A hydrocarbon mixture of the same composition as listed in Example 2 was conducted with a gradual addition of 2.0 mol-percent of hydrogen, at a pressure of 4 atmospheres gauge pressure, at the rate of 75 kg. per hour and at a hydrogenation temperature of approximately 100 to 110° C. over 9 liter of a catalyst which contained 9% of Cu, 3% of Ni and .4% of Cr on silica gel. The catalyst was prepared by impregnation of the carrier with the ammoniacal-aqueous solutions of the proper quantities of the carbonates, or formate of copper and nickel respectively and chromic acid, subsequent desiccation and reduction with hydrogen. The hydrocarbon mixture, upon leaving the furnace, had practically the same composition as the mixture obtained in case of Example 2, namely

	Mol percent
n-Butane -----	4.8
n-Butene-1 -----	63.5
Trans-butene-2 -----	18.7
Cis-butene-2 -----	11.4

with the remainder being other hydrocarbons. The butadiene-1,3 was reduced to less than .005 mol-percent.

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After 150 days of operation the activity and selectivity of the catalyst had changed only insignificantly.

Example 4

A hydrocarbon mixture with a content of

	Mol percent
n-Butane	6.5
n-Butene-1	23.5
Trans-butene-2	42.1
Cis-butene-2	24.3
Butadiene-1,3	.8

and approximately 2.8 mol-percent of other hydrocarbons was conducted, with gradual addition of 1.3 mol-percent of hydrogen, at a pressure of 4 atmospheres gauge pressure, at the rate of approximately 9 kg. per hour and at a hydrogenation temperature of 90 to 100° C. over 1 liter of a catalyst which was the same as that used in Example 3. The hydrocarbon mixture, upon leaving the hydrogenation furnace, had the following composition (disregarding the small quantity of hydrogen):

	Mol percent
n-Butane	6.5
n-Butene-1	24.3
Trans-butene-2	42.0
Cis-butene-2	24.4

with the remainder being other hydrocarbons. The butadiene-1,3 was reduced to less than .005 mol-percent.

Example 5

A hydrocarbon mixture containing 99.1 mol-percent of n-butene-1 and a .3 mol-percent of butadiene-1,3 with the remainder of .6 mol-percent consisting primarily of isobutene was conducted, with the gradual addition of .5 mol-percent of hydrogen, at a pressure of 4 atmospheres gauge pressure, at the rate of approximately 10 kg. per hour and at a hydrogenation temperature of 85 to 90° C. over 1 liter of a catalyst as described in Example 3. The hydrocarbon mixture leaving the hydrogenation furnace had (disregarding the small quantity of hydrogen) a content of 99.3 mol-percent of n-butene-1, the remainder being primarily isobutene. The butadiene-1,3 was reduced to less than .005 mol-percent.

The comparative Examples 1a and 2a below show that in the presence of copper-nickel catalysts with a quantitative relation thereof outside of the range of the present invention, the butene-1 is isomerized to a large degree into the undesirable butene-2.

Example 1a

A hydrocarbon mixture of the composition set forth in Example 2 was hydrogenated under the same conditions as given in the Example 2, the only difference being that the catalyst, while being prepared in the same manner, contained 10% of Ni, 2% of Cu and .3% of Cr on silica gel.

The hydrocarbon mixture, upon leaving the hydrogenation furnace, had the following composition (disregarding the small quantity of hydrogen):

	Mol percent
n-Butane	5.0
n-Butene-1	59.9
Trans-butene-2	20.9
Cis-butene-2	12.5
Butadiene-1,3	0.08

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with the remainder being other hydrocarbons. An isomerization of n-butene-1 to butene-2 was very apparent. Furthermore, butadiene-1,3 was not eliminated as extensively as in Example 2.

Example 2a

A hydrocarbon mixture of the composition set forth in Example 2 was hydrogenated under the same conditions as given in Example 2, the only difference being that the catalyst, while having been prepared in the same manner, contained 10% of Cu and .2% of Ni on silica gel. The hydrocarbon mixture, when leaving the hydrogenation furnace, had the following composition (disregarding the small quantity of hydrogen):

	Mol percent
n-Butane	4.8
n-Butene-1	62.3
Trans-butene-2	19.1
Cis-butene-2	11.7
Butadiene-1,3	.5

with the remainder being other hydrocarbon. The butadiene-1,3 was not removed.

When the hydrogenation temperature was raised to 150° C., the butadiene-1,3 content was reduced to .03 mol-percent while at the same time a very pronounced isomerization took place with a loss of butene-1.

The hydrocarbon mixture, upon leaving the furnace, had the following composition:

	Mol percent
n-Butane	5.1
Butene-1	56.4
Trans-butene-2	23.2
Cis-butene-2	13.7

with the remainder being other hydrocarbons.

I claim:

1. Method for the selective hydrogenation of butadiene-1,3 in a hydrocarbon mixture containing only a small amount of butadiene-1,3 and a much larger quantity of butene-1 which comprises hydrogenating said mixture at a temperature within the range 40° to 130° C., in the presence of a copper-nickel-containing carrier catalyst having a metal content of from 2 to 60 percent by weight and a copper-nickel ratio from 10:1 to 1:1, whereby the butadiene-1,3 of the mixture is selectively hydrogenated whilst isomerization of butene-1 is avoided.

2. Method according to claim 1 in which the catalyst contains a copper catalyst modifier in quantity from .05 to 15 percent by weight, relative to the total weight of the catalyst.

3. Method as defined in claim 1 in which the quantity of hydrogen used in the hydrogenation is at least chemically equivalent to the quantity of butadiene-1,3 in said mixture.

References Cited

UNITED STATES PATENTS

3,076,858 2/1963 Fravel et al. 260—677

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