

1

3,634,536

SELECTIVE HYDROGENATION OF ALKYNES

Ludo K. Frevel, Midland, and Leonard J. Kressley, Saginaw, Mich., assignors to The Dow Chemical Company, Midland, Mich.

No Drawing. Filed Apr. 27, 1970, Ser. No. 32,378

Int. Cl. C07c 7/00

U.S. Cl. 260—681.5 R

2 Claims

ABSTRACT OF THE DISCLOSURE

An improved process for selectively hydrogenating acetylenic impurities in an isoprene- or butadiene- containing stream whereby from 0.7 to 15 volume percent CO is utilized during normal hydrogenation over a copper-based catalyst.

BACKGROUND OF THE INVENTION

It is well known that a variety of processes for the pyrolysis of petroleum fractions produce relatively large quantities of diolefins, particularly conjugated diolefins. The diolefin-containing mixtures so obtained also contain other hydrocarbons. It is a common practice to fractionate this mixture to obtain, for instance, a fraction containing compounds such as butadiene-1,3, isobutane, isobutylene, n-butylene-1, n-butane, n-butylene-2, methylacetylene, ethylacetylene, vinylacetylene, and the like. Dehydrogenation of n-butane or n-butenes or both and 2-methyl butane or 2-methyl butenes to butadiene and isoprene, respectively, also produces some C₄ and C₅ acetylenic compounds which must be removed from the diene before use in polymerization reactions.

It has been the experience of the art that, while the diolefin content of each fraction may be concentrated by usual purification techniques, the acetylenic hydrocarbons and other highly unsaturated hydrocarbon impurities of about the same boiling point are extremely difficult to separate.

It is the current practice of industry to selectively hydrogenate the acetylenic and other unsaturated impurities in order to render them more amenable to standard removal procedures. However, two problems have been experienced by the art:

(1) A significant amount of butadiene or isoprene is lost during the selective hydrogenation; and

(2) The process, as practiced, is limited in the amount of acetylenics which may be removed, i.e., final acetylenic concentrations much below 100 p.p.m. by weight are difficult to achieve without excessive conversion of the diene to a monoolefin or alkane.

SUMMARY OF THE INVENTION

It has now been discovered that it is possible, in accordance with the method of the present invention, to correct the problems experienced by the art associated with the selective hydrogenation of acetylenic impurities in an isoprene- or butadiene-containing stream.

It is an object of the present invention to selectively hydrogenate the acetylenic compounds in an isoprene- or butadiene-containing stream without a material loss of the diene.

It is a further object to provide a process which effectively hydrogenates a greater proportion of acetylenic compounds than has heretofore been possible without a material loss of isoprene or butadiene.

Therefore, in accordance with the method of the present invention, it is now possible to reduce the concentration of C₂₋₅ acetylenes to a level as low as about 500

2

p.p.m. by selective hydrogenation, said process comprising passing an isoprene- or butadiene-containing stream with excess hydrogen, said stream containing up to about 1 weight percent of C₂₋₅ acetylenes, over a copper-based catalyst, said hydrogenation to occur in the presence of from 0.7 to 15 volume percent of CO.

Further, it is now possible, also in accordance with the present invention, to reduce the concentration of C₂₋₅ acetylenes to a level even as low as about 10 p.p.m. or less by selective hydrogenation, said process comprising passing an isoprene- or butadiene-containing stream with excess hydrogen, said stream containing 50 to 1000 p.p.m. of C₂₋₅ acetylenes, over a copper-based catalyst, said hydrogenation to occur in the presence of from 3% to 15 volume percent of CO.

The catalytic hydrogenation conditions and catalysts generally suitable for the method of this invention are detailed in U.S. Pat. 2,426,604 (1947), the specification of which is hereby expressly incorporated by reference. The streams which are suitable herein as feeds comprise those which contain isoprene or butadiene-1,3, and other hydrocarbons, such as isobutane, isobutylene, n-butylene-1, n-butane and n-butylene-2; up to 1 weight percent of C₂ acetylenic compounds, such as acetylene, methylacetylene, vinylacetylene, ethylacetylene, and the like; and, other hydrocarbon compounds such as alkanes and cycloalkanes, such as n-pentane, isopentane, neopentane, cyclohexane, and the like.

The catalysts which are suitable for the process of this invention are prepared so as to contain between 85 and 99.9 (preferably between 90 and 97) percent by weight of copper and between 15 and 0.1 (preferably between 10 and 3) percent of another metal, the oxide of which is reducible to a lower valence state with hydrogen at temperatures below 550° C. Examples of such metals include chromium, cobalt, manganese, nickel, vanadium, titanium, molybdenum, cadmium, zinc, silver, and the like, and also mixtures of such metals.

The catalysts are preferably employed in dispersed form on a substantially inert carrier material such as aluminum silicate, brick, stoneware, pumice, porous silica, and the like. Generally, this supported catalyst is prepared so as to contain from 10 to 30 percent by weight of the mixture of metals, but it may contain such metals in smaller or greater proportions. The above incorporated patent includes detailed instructions as to the various methods of preparing said catalyst.

The reaction conditions which are most suited for the method of this invention involve generally a 4 to 7 (preferably about 6) fold excess of hydrogen with respect to the concentration of acetylenes in the feed, and a space velocity of 300-1000, preferably about 600.

SPECIFIC EMBODIMENTS

Example I

The reactor was a glass tube (1.5 centimeters I.D. by 10.5 centimeters long) with a 3 millimeter O.D. thermocouple well centered concentrically the length of the tube. The internal volume of the reactor was 18.5 milliliters. It was loaded with 9.827 grams of catalyst. The catalyst contained 14 weight percent copper and 0.7 weight percent nickel on a siliceous support.

The reactor tube was inserted into a thermostatic heating unit, and the reactor brought to the indicated temperature. The feed stream was vaporized and mixed with hydrogen and carbon monoxide, and the mixture passed through the heated reactor. The effluent was condensed in a Dry Ice trap, the condensate being analyzed by gas liquid chromatography.

The specific conditions, results and analytical data are contained in the following table:

	1			2			3			4		
	Without CO			With CO, 0.48 vol. percent			With CO, 5.47 vol. percent			With CO, 0.74 vol. percent		
	Mole percent			Mole percent			Mole percent			Mole percent		
	Feed	Eff. ²	Percent ¹	Feed	Eff.	Percent	Feed	Eff.	Percent	Percent	Eff.	Percent
Compound:												
Total butanes.....	8.0	8.3	-----	9.29	9.20	-----	9.29	9.08	-----	9.17	9.13	-----
Total butenes.....	41.8	42.7	-----	53.10	54.22	-----	53.10	53.21	-----	52.45	52.17	-----
1,3-butadiene.....	50.2	49.0	-2.4	37.45	36.39	-2.8	37.45	37.55	+0.27	38.20	38.52	+0.84
Total C ₄ =(p.p.m.).....	(918)	(14)	-----	(1,215)	(Nil)	-----	(1,215)	(Nil)	-----	(3,300)	(590)	-----
Inlet temp., °C.....		179			180			180			149	
Outlet temp., °C.....		179			180			180			154	
H ₂ (vol. percent).....		0.87			0.72			0.72			0.98	
H ₂ /C ₄ =.....		9.5			6.0			6.0			3.0	

¹ Percent change (plus or minus) in butadiene. ² Effluent.

Example II

A further experiment under similar circumstances as above was conducted. The feed analysis was as follows:

	Liquid percent	
Isobutane	1.4	
Isobutylene	8.5	
n-Butylene-1	27.2	
Butadiene-1,3	50.8	
n-Butane	8.2	²⁵
n-Butylene-2 L.B.	3.9	
	Wt. percent	
Methyl acetylene0033	
Ethyl acetylene0076	³⁰
Vinyl acetylene0795	

A semi-continuous run was made with the object of demonstrating the effect of CO on the level of acetylenes remaining in the feed after hydrogenation.

210 ml./min. of the above hydrocarbons and 7.5 ml./min. of a 75%/25%-argon/hydrogen mixture were passed through the reaction chamber described above at a temperature of from 178-181° C. At the beginning about 12 volume percent of CO was also fed, and the acetylene levels monitored. After a period of time the CO flow was shut off, and the acetylenes monitored further. Finally 12 volume percent of CO was again admitted, and, once again, the acetylenes monitored.

It was noted that the acetylene concentration in the effluent was generally about 5 times greater when the

CO was not present during hydrogenation, concentrations as low as 7 p.p.m. being realized with the addition of CO.

An isoprene-containing stream would have the acetylenic impurities therein selectively hydrogenated similarly as above.

We claim:

1. In the process for the selective hydrogenation of acetylenic impurities in an isoprene- or butadiene-containing stream, said process comprising passing said isoprene- or butadiene-containing stream with excess hydrogen, said stream containing up to about 1 weight percent of C₂₋₅ acetylene compounds, over a copper-based catalyst, the improvement of carrying out said hydrogenation in the presence of from 0.7 to 15 volume percent based on the volume of said stream of CO.

2. The process of claim 1 wherein from 3 to 15 volume percent of CO is utilized.

References Cited

UNITED STATES PATENTS

3,076,858 2/1963 Frevel et al. 260-677

PAUL M. COUGHLAN, JR., Primary Examiner

V. O'KEEFE, Assistant Examiner

U.S. Cl. X.R.

260-677 H