United States Patent Office

3,113,983

Patented Dec. 10, 1963

3,113,983

SELECTIVE HYDROGENATION OF DIOLEFINS

Francis William Kirsch, Wilmington, Del., and Samuel E. Shull, Media, Pa., assignors to Air Products and Chemicals, Inc., a corporation of Delaware

No Drawing. Filed Apr. 7, 1959, Ser. No. 804,583

6 Claims. (Cl. 260—677)

The present invention relates to selective hydrogenation of diolefins in hydrocarbon streams containing monoolefins and is especially concerned with selective conversion of butadiene contaminant in butene charge stocks employed in alkylation processes for production of aviation and motor gasoline. The invention, in certain of its aspects, also is applicable to selective conversion of diolefins, particularly C_4 diolefins, to monoolefins; as for example in production of butylenes for use in synthetic "Butyl" rubber or for other uses.

The C_4 fraction employed in alkylation processes is principally that obtained from thermal or catalytic cracking of higher boiling hydrocarbons or from a hydrocarbon coking operation; the C_4 cut is taken over a practical boiling range so as to be substantially free of C_3 and C_5 hydrocarbons, although minor amounts of these may be present by entrainment or otherwise. Such C_4 fraction may generally contain in the order of about 0.3 percent and up to about 1 percent or more by weight of diolefin; the C_4 fraction from a cracking operation rarely contains as much as 2 percent of diolefin. Even this small content of diolefin in the feed for the alkylation process has been widely recognized as being extremely undesirable for the one reason, among others, of the greatly increased consumption of acid made necessary thereby, as a result of forming tarry acid-diolefin condensation products, adversely affecting the over-all economics of the alkylation process. Several suggestions for the conversion or removal of the diolefins from hydrocarbon mixtures also containing monoolefins have not proved attractive, because of accompanying concomitant disproportionate loss of monoolefins in the treated product, and high operating and investment costs.

In the case of a C_4 fraction derived from a coking operation which may contain even higher proportions of diolefins, going up to 5% or more, the problem is even more acute, and the use of such fractions for alkylation has been largely avoided.

Among the objects of the present invention is the provision of an improved process for selective conversion of C_4 or C_5 diolefins in a monoolefin-rich hydrocarbon fraction, wherein the monoolefin content is about 5 or more times the diolefin content, by catalytic hydrogenation of diolefins to more saturated product and with minimum hydrogenation of monoolefins in such fraction.

Such selective conversion of the diolefins is accomplished, in accordance with the present invention, by effecting the hydrogenation over a selected catalyst and under carefully controlled operating conditions. By this controlled operation the butadiene content of a C_4-olefin-containing fraction can be lowered to 0.1 weight percent or less and with no net loss of butenes in most instances or under adverse conditions at a maximum net loss of less than about 1 percent of butenes.

The process of the invention involves passing of a

narrow boiling hydrocarbon fraction comprising C_4 or C_5 monoolefins and which contains a minor quantity of diolefins, over catalyst comprising sulfided cobalt molybdate on alumina carrier; such hydrogenation being effected at a temperature in the range of about 200 to 700° F., and at pressures of about 1 to 25 atmospheres. The hydrogen added in the process is maintained at least in excess of the stoichiometric requirement for full conversion of the diolefins to monoolefins. In practice generally as applied, for example, to selective hydrogenation of an olefinic C_4 fraction containing up to about 2 percent by weight diolefins, hydrogen is employed in a ratio of at least about 3 mols per mol of diene in the hydrocarbon feed and generally not in excess of about 40/1. Space rate of hydrocarbon feed may be from about 1 to 20 volumes of hydrocarbon (determined as liquid) per hour per volume of the catalyst in the reactor.

Substantially the same reaction conditions as above described in the case of C_4 hydrocarbons, are applicable to the treatment of C_5 hydrocarbon mixtures comprising a small quantity of C_5 diolefins, operating preferably in the higher portion of the described temperature range for volatilizing the charge and to effect reaction in shorter contact time to avoid polymer formation.

While the greatest advantages of the described process are obtained in the treatment of olefinic C_4 hydrocarbon streams containing less than about 2% butadiene by weight of total hydrocarbons, the process is also applicable, but not necessarily with equal results, to the treatment of olefinic C_4 fractions of higher diolefin content, such as a butane-butylene fraction obtained from a thermal coking operation which may include up to about 5–6% diolefins. A further application of the invention lies in the treatment of a butylene-rich stream from a dehydrogenation process containing from a fraction of a percent up to about 5% diolefin. For example, in the dehydrogenation of butane, for production of butadiene, particularly after separation of the product butadiene by fractionation and extraction, there still remains in the monoolefin-rich raffinate a small percentage of butadiene of from about a fraction of a percent up to about 2%, depending upon the efficiency of the separation. This small amount of butadiene cannot be economically recovered as such, and interferes with the possible uses of the raffinate, for instance as feed to alkylation. Some butadiene is also produced in those processes designed principally for conversion of butane to butene. If the quantity of butadiene in the product is sufficiently great, say in excess of about 5%, its recovery by known procedures may be warranted. Smaller quantities of butadiene, as between about 3 to 5% may or may not be worth recovering as such, depending upon recovery costs versus market demand and value. In either of the above instances, the enhancement of the butene product by selective hydrogenation of diolefins in accordance with the present invention, comes into consideration.

The selective hydrogenation of butadiene in a monoolefin-rich mixture by the present invention is more easily accomplished and with greatest efficiency when the proportion of diolefin in the mixture is quite low, for example less than about 2%. In such instance catalytic hydrogenation under the described operating conditions can be accomplished in isothermal or adiabatic reactor systems, and some variation from the optimum in process

variables can be tolerated at the expense of some sacrifice in yield and purity of product.

The catalyst employed may be commercial alumina-supported "cobalt molybdate" which has been sulfided, and which contains prior to sulfidation a total of about 8 to 18% by weight of the oxides of molybdenum and cobalt in the approximate weight ratio of about 4/1 to 5/1 (MoO_3/CoO). The designation "cobalt molybdate" is herein employed consistent with the terminology of the art, as embracing those catalysts containing metallic cobalt or an oxide thereof together with one or more oxides of molybdenum, and without regard as to whether a true chemical combination or complex is formed between the cobalt and molybdenum components which can be formulated as $CoMoO_4$. The sulfided catalyst accordingly may contain such distinguishable compounds as $CoS \cdot MoS_3$ together with partially sulfided derivatives of the starting cobalt and molybdenum oxides. The catalysts preferred in practice of the invention are those containing at all times during use at least one atom of sulfur for each atom of cobalt and for each atom of molybdenum. In fresh state when initially put to use the preferred catalysts are fully sulfided to at least the state of $CoS \cdot MoS_2$, with combined oxygen left only in the alumina carrier. Thus for a cobalt molybdate catalyst which prior to sulfidation contains 15% MoO_3 and 3% CoO the minimum sulfur content of the freshly sulfided catalyst will be about 7.8% by weight.

Numerous methods are described in the prior art for preparation of supported cobalt molybdate type catalysts, including among these separate impregnation of the carrier with a decomposable cobalt salt (nitrate) and with a decomposable molybdate (ammonium) with separate or simultaneous heat treatment to effect conversion of the salts to the corresponding oxides. The preferred carrier in these catalysts is a porous alumina such as so-called "activated alumina" or the various forms of gamma alumina.

A preferred method for preparation of superior cobalt molybdate on alumina catalyst involves impregnation of the porous alumina carrier with an aqueous ethylene diamine solution of the compounds of cobalt and of molybdenum, followed by drying and calcination.

The cobalt molybdate catalyst may contain small amounts of a promoter, such as about 1–3% nickel or of chromium oxide. These promoters can be incorporated in the alumina base by known impregnation techniques prior to sulfiding the catalyst.

The preferred operating range for selective hydrogenation of C_4 diolefin over the alumina-supported catalyst includes temperatures in the order of 250–500° F. and pressures of from about 150 to 300 p.s.i.g., employing hydrocarbon space rates from about one volume (determined as liquid) per hour per volume of catalyst upward, as up to about 12. Hydrogen is added in excess of the stoichiometric requirement for conversion of the diolefin to monoolefin as from 3 mols H_2 per mol diolefins in the charge up to about 40:1.

To obtain best results and longest useful life thereof, the catalyst must be kept in sulfided state so that the sulfur/Co+Mo mol ratio does not fall below about 3/1. To do this, there should be maintained in the catalytic hydrogenation zone a partial pressure of H_2S at no less than about $1/500$ of the hydrogen partial pressure at the lower temperatures of the described operating range and an increased ratio of the partial pressure of hydrogen sulfide to hydrogen at higher operating temperatures. While these quantities of hydrogen sulfide are in considerable excess of theoretical equilibrium requirements, a content of 0.005 to 0.01% H_2S by weight of hydrocarbon in the feed should generally be sufficient to provide the required partial pressure of hydrogen sulfide in the reactor to maintain the catalyst in its desired state of sulfidation when operating with the catalysts above described over the range of hydrogenation conditions indicated. If the feed stock does not contain sufficient sulfur (available as H_2S in the hydrogenating reactor) to maintain the catalyst in sulfided state, then supplementary sulfide should be added with the charge preferably in the form of hydrogen sulfide in amount sufficient to maintain the sulfided state of the catalyst under the operating conditions employed, and within the minimum limits indicated above. While practical considerations dictate that the amount of added sulfide should be kept as low as possible consistent with maintaining the catalyst in active state, no untoward effects have been observed from the presence of much larger quantities of sulfur, since the catalyst is not sensitive thereto. To avoid excessive dilution of the charge and to keep the handling problem within practical limits, the sulfide addition should best be kept below about 1% by weight of the hydrocarbon charge.

EXAMPLE I

In order to compare the results obtained in selective hydrogenation over sulfided and non-sulfided catalyst, the following runs were made using each of the catalysts at the same conditions on a feed stock composed of: (mol percent) 49.4% butenes, 38.7% butane, 0.34% butadiene, 11.6% pentane; and containing 0.006% by weight sulfur. In each of the runs made the operation was carried out at 500° F., atmospheric pressure, and at a liquid hourly space velocity of 3 (vol. hydrocarbon/vol. catalyst); 5 mol percent hydrogen being introduced with the feed. The results are reported in Table 1 below:

Table 1

Hours of Operation	Residual Butadiene—mol Percent Hydrocarbon Charge	
	(B) Sulfided Catalyst	(A) Non-Sulfided Catalyst
1		0.00
2	0.00	
3		0.08
5	0.00	
8		0.09
10		0.13
11	0.00	
15	0.00	

These data indicate that the sulfided catalyst maintains activity for butadiene hydrogenation over a significantly longer period than the non-sulfided catalyst.

Catalyst A used in the above runs was prepared by placing in a Lancaster mixer 336 parts by weight of hydrated alumina (73% Al_2O_3) and pouring thereover the ammonium molybdate solution (containing 45.5 parts MoO_3 and 45.5 parts water) and the solution of a cobalt nitrate ethylene diamine complex [containing 35 parts $Co(NO_3)_2 \cdot 6H_2O$, 21 parts ethylene diamine, and 7 parts water]. Approximately 35 to 38 parts water were added to obtain an extrudable mix and the mixture was mulled for 30 minutes and extruded to pellet form. The wet pellets were dried for 20 minutes on a belt at 250–265° F. and then calcined in air at 1000–1050° F.

Catalyst B was prepared by sulfiding pellets of catalyst A for three hours at 800° F. in an atmosphere of 75% N (vol.), 25% H_2S, followed by nitrogen purge.

EXAMPLE II

The selectivity and stable activity of the sulfided catalyst will be seen from the following runs made on a feed stock composed of: (mol percent) 37.6% butenes, 55.9% butanes, 1.3% butadiene, 5.2% C_3+C_5; and containing 0.008% by weight sulfur. The operation was carried out at a pressure of 150 p.s.i.g., and at a liquid hourly space velocity (LHSV) of 12 (vol. HC per hour

per vol. cat.) with 10 mol percent hydrogen added to the feed, starting initially at a temperature of 500° F. and then lowering temperature as indicated in Table 2 below. A fresh sample of the same catalyst was employed as in Example I (B) above.

Table 2

Hours Run	Residual Butadiene (mol Percent)	Net Butene Production [a] (mol Percent)
185	0.00	−2.4
215	0.00	−0.5
253	0.03	−0.4
257	0.03	−1.6
Temp. Lowered to 450° F.:		
258	0.11	+0.3
275	0.22	+0.1
277	0.18	−1.6
281	0.33	−0.3
298	0.38	0.0

[a] In the above and subsequent tables, positive values for butene production mean a net gain from hydrogenation of butadiene less butenes lost by hydrogenation to butanes; negative values mean that more butenes were hydrogenated to butanes than were gained from butadiene hydrogenation.

At the conclusion of the above life study runs, the spent catalyst was analyzed and showed a sulfur content of 5.84%. Since the original catalyst contained 9.39% sulfur, it appears that nature and quantity of the natural sulfur content of the hydrocarbon feed in this instance was insufficient to maintain the original sulfided state of the catalyst under the described operating conditions.

While good results were obtained at the higher temperature (500° F.), it is preferred in commercial operations to employ lowest practical temperature consistent with acceptable results not only because of savings in heating costs but also doing away with the need for expensive heat resistant alloys in the lines and vessels handling the charge and products. Accordingly, a number of runs were made to determine the feasibility of lower temperature operation.

EXAMPLE III

Using another sample of the same sulfided catalyst as in the previous Example II and the same charge stock there described, a number of runs were made at the temperatures and other operating conditions reported in Table 3 below, at a nominal 10 mol percent hydrogen in the feed.

Table 3

Temp. (° F.)	Time (hrs.)	Press (p.s.i.g.)	LHSV	Residual Butadiene (mol Percent)	Butenes Production (mol Percent)
350	4	150	1	0.00	
300	6	150	1	0.00	
250	12	200	1	0.00	−1.0
250	15	200	3	0.15	−1.1
250	24	250	3	0.07	+1.1

A life test run was made under preferred operating conditions on a charge similar to that reported in Example III above, as follows:

EXAMPLE IV

The charge was composed of (mol percent): 37.5% butenes, 56.2% butanes, 1.3% butadiene, 5.0% C_3+C_5; and contained 0.008 weight percent sulfur. The operation was carried out at 250° F., 250 p.s.i.g., 2 LHSV, with 10 mol percent H_2 in the feed, and the effluent product analyzed periodically showing the following results:

Table 4

Cumulative Time (hrs.)	Residual Butadiene (mol Percent)	Butene Production (mol Percent)
2	0.00	+0.5
28	0.00	+1.1
67	0.00	−0.6
69	0.00	−0.5
98	0.05	−0.2
120	0.00	+1.4
140	0.12	+1.2
163	0.23	0.0
235	0.31	+0.9
240	0.20	−1.2
292	0.16	+0.7

After 70 hours and up to 100 hours of operation the amount of residual butadiene in the effluent has varied between 0 to 0.1 mol percent and was quite satisfactory, while the butene production remained at between about +1% to about −1%.

The above data indicate that low temperature operation is possible over the sulfided cobalt molybdate catalyst obtaining selective hydrogenation of the diolefins over a period of about one week of continuous operation.

The importance of maintaining the catalyst in sulfided state for obtaining best selectivity in hydrogenation of the diolefin over extended periods of operation, will be evident from the following runs.

EXAMPLE V

A C_4 hydrocarbon fraction comprising (mol percent) approximately 50% butanes, 40% butenes, 1% butadiene and 9% C_3 hydrocarbons, and containing 0.02% by weight organic sulfur (predominantly methyl mercaptan) was passed over sulfided cobalt molybdate catalyst as described in Example I (B) above. The operation was carried out at 300° F., 250 p.s.i.g., and 2 LHSV (hourly space velocity as liquid volume), with 10 mol percent H_2 added to the feed. Samples of the effluent product were analyzed periodically during the run, showing the results tabulated below:

Table 5

Cumulative Time (hrs.)	Residual Butadiene (mol percent)	Net Butene Production (mol percent)
24	0.00	−2.3
41	0.00	−0.1
48	0.00	−2.9
68	0.00	−1.4
140	0.05	−0.9
158	0.07	−0.9
163	0.14	+1.0
207	0.14	−0.3
307	0.29	−0.4
359	0.47	+0.9

Analysis of the effluent indicated that most of the organic sulfur in the charge had passed through the hydrogenation reactor substantially unchanged.

In another series of runs there was added to the same hydrocarbon charge stock of the example 0.02% by weight H_2S and the mixture passed over the described catalyst under the same operating conditions as before (except for temperature increase noted below). Selective hydrogenation of the butadiene was obtained over an extended operating period beyond 6 weeks with no loss appearing in catalyst activity as shown by the results tabulated below at the 325° F. operating temperature:

Table 6

Temp. (° F.)	Cumulative Time (hrs.)	Residual Butadiene (mol percent)	Net Butene Production (mol percent)
300	629	0.02	+0.5
	705	0.03	+0.4
	795	0.07	+0.5
	812	0.14	+1.5
	815	0.12	+1.3
325	838	0.04	+1.2
	861	0.00	+0.6
	886	0.00	+0.7
	928	0.00	+1.7
	1,047	0.00	+0.5

Since no loss in catalyst activity or selectivity was observed after 1700 hours of continuous operation, it was predicted that in practice 6 to 8 months of continuous uninterrupted operation can be expected without necessitating regeneration or reactivation of the catalyst.

Once the catalyst in use has been reduced too far in sulfur content, acompanied by accumulation of carbonaceous deposit apparently resulting from polymerization of unsaturates, one cannot restore activity by resulfiding alone or by increasing the H_2S content of the feed. The catalyst may be regenerated, if desired, by oxidative combustion of the carbonaceous deposit and then resulfided with H_2S prior to being put on stream. It may be preferred, however, after an extensive period of use, to replace the deactivated catalyst with fresh sulfided catalyst.

In operation of the process care should be exercised in minimizing sulfidation of the olefins by possible reaction with H_2S to form mercaptans. Such reaction of the olefins is largely or entirely avoided by limiting H_2S in the reaction zone to no more than about 1% by weight of unsaturated hydrocarbons in the charge and by avoiding the presence of oxygen-containing compounds in the reaction zone that may tend to promote sulfidation of the olefins. Thus, addition of steam in the process is best avoided, and the water content of the hydrocarbon charge should be below about 100 parts per million. Ordinary refinery C_4 and C_5 streams are sufficiently dry as to require no special drying treatment.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. The method of selectively hydrogenating diolefins present in minor quantity in a mixed hydrocarbon stream boiling chiefly in the C_4 to C_5 range and also containing monoolefins in an amount of at least 5 times that of the diolefins, which method comprises passing said mixed hydrocarbon stream together with hydrogen through a reaction zone containing sulfided cobalt molybdate catalyst, at a temperature in the range of 200–700° F., while maintaining in said reaction zone a partial pressure of hydrogen sulfide at least sufficient to maintain the catalyst in sulfided state and not in excess of 1% by weight of unsaturated hydrocarbons in the mixed hydrocarbon stream.

2. The method of selectively hydrogenating diolefins contained in amount of up to about 2% by weight in a C_4 to C_5 hydrocarbon stream rich in butenes throughout prolonged periods of operation, which method comprises passing such hydrocarbon stream at 200–700° F. into contact with catalyst in a reaction zone together with 3 to 40 mols hydrogen per mol of diolefins in said stream, said catalyst comprising sulfided cobalt molybdate containing prior to sulfidation 8 to 18% of the oxides of cobalt and molybdenum supported on alumina, said oxides being in the weight ratio corresponding to 4/1 to 5/1 MoO_3/CoO, the sulfur content of the catalyst at all times during said contact with hydrocarbons being maintained to provide at least one atom of sulfur for each atom of cobalt and for each atom of molybdenum therein, the catalyst being maintained in such sulfided state by providing an environment of hydrogen sulfide in said reaction zone at a partial pressure which is at least $\frac{1}{500}$ of the hydrogen partial pressure in said zone.

3. The method of purifying a butene stream for use in alkylation to remove small amounts of diolefins present therein, which method comprises selectively hydrogenating said diolefins by contacting the butene stream containing the same with catalyst in a reaction zone together with at least 3 and up to 40 mols hydrogen per mol of diolefin and in the presence of hydrogen sulfide present in an amount of at least 0.005% by weight of total hydrocarbons in said butene stream, said hydrogenating being effected at a temperature in the range of 250–500° F. and at a pressure of 150–300 p.s.i.g., and said catalyst comprising sulfided cobalt molybdate on an alumina carrier.

4. The method according to claim 3 wherein said hydrogenating is effected at 300–325° F. with 10 mol percent hydrogen in the hydrocarbon feed, an amount of H_2S therein providing 0.02% by weight sulfur.

5. The method of selectively hydrogenating butadiene present in quantities of up to about 5% by weight in a mixed hydrocarbon stream of predominantly C_4 hydrocarbons and rich in C_4 monoolefins, which method consists essentially of: preparing a charge mixture of said hydrocarbon stream with from 3 to 40 mols of hydrogen per mol of butadiene in the charge and with at least $\frac{1}{500}$ mol of hydrogen sulfide per mol of hydrogen, the hydrogen sulfide concentration being less than 1% of the hydrocarbon stream; contacting said charge at temperatures in the range of 250–500° F. and pressures of 150 to 300 pounds per square inch gauge in a reaction zone containing sulfided cobalt molybdate catalyst supported on porous alumina; and withdrawing from the reaction zone a hydrocarbon stream containing less than 0.1 mol percent residual butadiene.

6. The method of selectively hydrogenating diolefins in a normally gaseous olefin stream which consists essentially of the steps of: preparing a catalyst consisting essentially of sorptive alumina and catalytic amounts of the oxides of cobalt and molybdenum; subjecting the catalyst of alumina and oxides of cobalt and molybdenum to sulfiding treatment consisting essentially of treatment with a hydrogen sulfide rich gas stream at a temperature of about 800° F. for about three hours to provide a sulfided cobalt molybdate catalyst; preparing a gas mixture consisting essentially of the hydrocarbon gas stream to be purified, hydrogen in a molar quantity from 3 to 40 times that of the diolefin and hydrogen sulfide in a quantity less than 1% of the hydrocarbon gas stream but more than one mol of hydrogen sulfide per 500 mols of hydrogen; directing the gas mixture at a temperature of at least 250° F. at a space rate greater than 1 liquid volume of hydrocarbon per volume of catalyst per hour at super-atmospheric pressure through a bed of said catalyst throughout an operating period of more than one thousand hours prior to the deactivation of the catalyst.

References Cited in the file of this patent

UNITED STATES PATENTS

2,458,980	Cole	Jan. 11, 1949
2,905,636	Watkins et al.	Sept. 22, 1959
2,914,470	Johnson et al.	Nov. 24, 1959
2,934,574	Viland	Apr. 26, 1960

FOREIGN PATENTS

427,632	Great Britain	Apr. 23, 1935