United States Patent Office

3,215,750
Patented Nov. 2, 1965

3,215,750

HYDROGENATION PROCESS FOR CONVERTING POLYOLEFINS OR ACETYLENES TO MONOOLEFINS

Hans A. Benesi, Berkeley, Calif., assignor to Shell Oil Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed Dec. 31, 1962, Ser. No. 248,215
6 Claims. (Cl. 260—683)

This invention relates to the hydrogenation of hydrocarbons having a plurality of olefinic and/or acetylenic bonds to the corresponding monoolefinic hydrocarbons by partial hydrogenation. More particularly, the invention relates to the selective hydrogenation of diolefins to monoolefins without substantial production of saturated compounds.

Diolefins are contained in various concentrations in gasoline fractions obtained from the thermal or catalytic cracking of higher boiling hydrocarbons. For example, a C_4 fraction from a catalytic cracking process may generally contain on the order of about 0.1% and up to about 1% or more of diolefins. A C_4 fraction derived from a fluid coking operation may contain as much as 5% or more diolefins. Gasoline fractions obtained from steam cracking naphtha fractions are highty unsaturated.

The presence of diolefins in gasoline fractions is generally undesirable for several reasons. Diolefins in gasoline have a pronounced tendency to polymerize, particularly under the influence of air and light, to form gummy materials which deposit upon feed lines, carburetors, valves and the like when the fuel containing them is used in internal combustion engines, and thus interferes with the proper operation thereof. The presence of diolefins in a C_4 or C_5 feed fraction to an alkylation unit is considered highly undesirable because of excessive acid consumption resulting from the formation of tarry acid-diolefin condensation products. The excessive acid consumption attributable to butadiene can be estimated by figuring that each gallon of butadiene contaminates or spends about 58 pounds of fresh acid from 98 pounds to 90% H_2SO_4. On the other hand, butene alkylate is made in some plants with acid consumption as low as 0.25 pounds per gallon of alkylate.

The detrimental effect of diolefins in gasoline fractions has supplied considerable incentive to find means for removing the diolefins or for converting them to unharmful compounds. Methods proposed heretofor have been to precontact the diolefin-containing gasoline fractions with such materials as acid clays, phosphoric acid or dilute sulfuric acid to polymerize selectively the diolefins which can then be removed conveniently by such means as fractional distillation. Such means are generally undesirable for such reasons as large volumetric hydrocarbon losses, large chemical losses, disposal problems for spend clay or acid, and the like. To avoid these problems, it has generally been of more interest to convert the diolefins to less harmful compounds such as by hydrogenation. Complete hydrogenation to form the corresponding saturated compound can be effected but partial saturation to the corresponding monoolefins is generally preferred. The monoolefins are generally desired for further processing, have a higher research octane number than the corresponding paraffin and, moreover, complete saturation would result in high hydrogen cost. Many catalysts have been proposed for selective hydrogenation of diolefins to monoolefins such as, for example, nickel sulfide, molybdenum sulfide, cobalt molybdate, copper chromite and the like. Such processes have been unsatisfactory for various reasons such as high catalyst cost, low activity, poor selectivity and poor catalyst stability.

It has now been found that diolefins and other highly reactive unsaturated compounds such as occur in light hydrocarbon oils obtained by cracking can be hydrogenated in a particularly selective manner to form monoolefins by using a catalyst comprising a metal of Group IB of the periodic table (Handbook of Chemistry and Physics, 44th Ed., pages 448–449), supported on an inert gel carrier such as silica gel. These catalysts are not only active but are highly selective. By light cracked hydrocarbon oils it is meant those hydrocarbon oils boiling from about C_3 to a final boiling point (ASTM) of about 420° F. which are obtained from cracking processes. This includes full boiling range gasoline or narrow fractions such as a C_4 or C_5 fraction. In addition, the process is suitable for converting diolefins-rich streams to monoolefins, such as excess butadiene or isoprene from polybutadiene or polyisoprene processes.

The Group IB metal is incorporated on a porous relatively inert gel support such as silica, the resulting catalyst being characterized by relatively high surface area, high selectivity, and high activity. While Group IB metals can be incorporated on silica gel by impregnation of the gel with an aqueous solution of a metal salt, superior catalysts are prepared by using a solution wherein the metal is complexed with a nitrogen base which can be subsequently removed by calcining the catalyst at a temperature which is otherwise not detrimental to the catalyst. Particularly suitable are solutions wherein the metal salt is complexed with a nitrogen base, such as ammoniacal solution of metal salts. By ammoniacal solution is meant those containing excess ammonia or other complexing agents, such as the organic amines, e.g. ethylene diamine and the like. Since aqueous solutions of the metal salt are used, the organic amine should be water soluble. The metal salt solution should contain enough or amine to form a complex with the metal ions and thus prevent precipitation of the metal as a metal hydroxide. The ammonia or amine concentration varies with the nature and concentration of the metal ion. Thus, with 0.1 M $AgNO_3$, an ammonia concentration of 0.5 M or higher is required; with 0.2 M $Cu(NO_3)_2$ an ammonia concentration of 3 M or higher is required. In general the molar ratio of ammonia to metal should be 2/1, preferably 4/1 or higher. A higher ratio is used with copper than with silver. For strong complexing agents such as a diamine, lower ratios can be used than with ammonia. For example, ethylene diamine, can be used in about 1/2 the ratio used with ammonia. Contacting the silica gel with the ammoniacal solution of the Group IB metal salt for a period of up to 2 to 3 hours is generally sufficient, although longer times can be used if desired. Since silica gel is attacked by strongly alkaline solution the time of contact should not be excessive. The Group IB metal is incorporated on the carrier in an amount (calculated as metal) from about 1 to 15% by weight and preferably from 3 to 10% by weight based on the total catalyst.

The selective hydrogenation is carried out at a temperature in the range from about 100 to 650° F. and preferably 200 to 500° F. The operation is conducted at pressure of from about 1 to 50 atm.

The hydrogenation can be carried out in vapor phase, liquid phase, or as a mixed vapor-liquid phase. Because of the exothermic nature of the hydrogenating reactions there may be an increase in temperature in the catalyst bed. Therefore, it is of particular advantage to operate in the liquid phase since because of the higher specific heat of the liquid there will generally be smaller rises in temperature than when operating in the gaseous phase. If desired, diluents can be introduced to the reaction zone to absorb heat liberated by the reaction.

To assure satisfactory hydrogenation, hydrogen is added in an amount at least equal to the stoichiometric requirement for the conversion of the diolefin to monoolefin to up to 10 times or more of the theoretical amount. It is preferred to use from 2 to 5 times the theoretical amount.

The gas employed can be substantially pure hydrogen or a hydrogen-containing gas mixture, such as a mixture of hydrogen and light hydrocarbons. The gases should preferably contain more than 60% by volume of hydrogen. Suitable gases are, for example, the hydrogen-containing gases obtained in the catalytic reforming of gasoline fractions. When using an excess of hydrogen, it is of advantage to recycle the hydrogen used, preferably after the previous removal of undesired components such as any hydrogen sulfide formed during the hydrogenation.

The liquid hourly space velocity (weight of diolefin per hour per unit weight of catalyst) employed can vary over a wide range such as about 0.5 to 300 or higher. High space velocities, e.g. about 1 to 300, preferably 1 to 100 can be used with copper catalysts, which are very active; however, copper loses activity during the hydrogenation reaction, presumably as a result of carbonaceous deposits on the catalyst formed by polymerization of the diolefin. The silver catalyst, which is less active than copper is remarkably more stable than the copper catalyst. Space velocities of about 0.5 to 30, preferably about 1 to 10 are used with silver. The high space velocities which can be used with the present catalysts allow the use of small reactors and a small catalyst inventory, important factors in determining process costs. The high activity also permits the use of relatively low temperatures. In general, low temperatures can be used at low space velocities while higher temperatures are required at higher space velocities.

EXAMPLE I

Various catalysts were prepared using silica gel (Davison Chemical Company, grade 70, 60 to 200 mesh) as a support. The silica gel contained 0.02% by weight aluminum and had a surface area of 370 sq. mg./g. and a pore volume of 0.79 cc./g. Catalyst A was prepared by adding 200 ml. of 0.1 M copper nitrate to 200 ml. of 1 M ammonium hydroxide. To the above solution were added 30 grams of silica gel with stirring. Stirring was continued for 5 minutes after the silica gel addition. The solids were permitted to settle and excess solution was decanted. The solids were washed twice with distilled water by decantation and the catalyst dried overnight at 120° C. Catalyst B is prepared similarly. In this case the ammoniacal solution consist of 200 ml. of 0.1 M silver nitrate and 80 ml. 1 M ammonium hydroxide. To increase the content of metal in the catalyst the procedure can be repeated using the dried product in place of silica gel. Catalyst C, a copper catalyst, and Catalyst D, a silver catalyst, were prepared by a conventional impregnation method. In this method an appropriate volume of a 1 M solution of the metal nitrate is added to 10 g. of silica gel. Enough distilled water is added to make a viscous slurry. The slurry is evaporated to near dryness, with constant stirring, and dried overnight at 120° C. Before use, the catalysts were reduced in a stream of hydrogen for about 30 minutes at a temperature of 575° F. for copper and 750° F. for silver.

The above catalysts were tested for the selective hydrogenation of isoprene (2-methylbutadiene-1,3) at a temperature of 437° F. (225° C.) atmospheric pressure and a hydrogen to oil mole ratio of 3 to 1. The results are given in Table I below.

Table I

Catalyst	Metal Content, percent weight	WHSV	Conversion, percent weight
A	3.7	134	100
C	3.6	67	62
B	7.7	3.2	99
D	6.9	3.3	33

Conversion given for the copper catalysts A and C is the initial conversion since at this temperature conversion dropped rapidly with time, presumably because of excessive polymerization of isoprene on the catalyst. The space velocity (WHSV) is expressed as weight of isoprene per hour per unit weight of catalyst. Selectivity in each case was 100%, i.e. isoprene was converted to isoamylene.

EXAMPLE II

The highly active copper and a silver catalyst similar to Catalyst B in Example I was subjected to additional tests wherein the weight hourly space velocity was varied over a considerable range, the pressure, temperature and hydrogen rate being the same as that employed in Example I. The silver catalyst contained 7.1% w. silver and is designated as Catalyst E. Again the conversion for the copper catalyst is the initial conversion as activity declined rapidly. Selectively was 100% at each conversion, i.e. all the isoprene converted was to isoamylene. The results are given in Table II.

Table II

Catalyst	WHSV	Isoprene Conversion, Percent By Weight
A	299	29.1
A	255	49.0
A	134	91.2
E	33	12.2
E	16.5	34.6
E	8.2	51.7
E	1.6	99.8

EXAMPLE III

A nickel catalyst was prepared by impregnating silica gel with nickel nitrate solution in the manner described for the impregnated copper and silver catalyst of Example I. This nickel catalyst is designated as Catalyst F and contains 3.2% w. nickel. The catalyst was reduced with hydrogen for 30 minutes at 750° F. before use. Catalysts A, E, and F were tested in the hydrogenation of isoprene at atmospheric pressure and a molar ratio of hydrogen feed of 3 to 1. The results are presented in Table III.

Table III

Catalyst	WHSV	Temperature, ° F.	Contact Time, min.	Product Composition, percent w.		
				Unreacted Isoprene	Isoamylene	Isopentane
F	657	437	1.5	18.0	45.2	36.8
F	657	437	2.5	28.9	49.8	41.3
A	255	437	5	61.0	48.9	0.1
A	255	437	31	92.2	7.7	0.1
A	255	437	37	95.3	5.6	0.1
E	13.4	455	5	53.7	46.3	0
E	13.4	455	20	54.5	45.5	0
E	13.4	455	35.0	58.0	42.0	0

In a further test the nickel catalyst was sulfided with thiophene. At a WHSV of 13 and 437° F. reactor temperature, and other conditions being the same, only 6% by weight of isoprene was converted, although selectivity was 100%.

EXAMPLE IV

An impregnated platinum catalyst was prepared using 0.2 M solution of H_2PtCl_6 in place of metal nitrate solution. The finished catalyst, reduced in hydrogen at 400° F., contained 0.5% platinum. This platinum catalyst, Catalyst G, was compared with silver Catalyst E in experiments in the hydrogenation of isoprene and 2-methyl-1-butene at 437° F. (225° C.). In the hydrogenation of isoprene, space velocity was varied over a wide range and hydrogen consumption was measured. With the platinum catalyst, hydrogen consumption increased as space velocity was reduced, hydrogen consumption varying from about 0.2 to 1.3 moles of hydrogen per mole of isoprene. Hydrogen consumption in excess of 1.0 is indicative that isoprene is being converted to isopentane. With the silver catalyst, hydrogen consumption increased to 1.0 as space velocity was lowered, and remained at this value even with further reductions in space velocity. This indicates that the silver catalyst is highly selective and that the reaction virtually ceases when 1 molecule of hydrogen has reacted with one mole of isoprene.

In the hydrogenation of 3-methyl-1-butene (at atmospheric pressure and 1/1 H_2/oil), conversion to isopentane was only 0.5% with the silver catalyst at a WHSV of 2.0 whereas the conversion was 29.6% with the platinum catalyst even at the extremely high space velocity of about 14,000.

I claim as my invention:

1. A process for hydrogenating a diolefin to a monoolefin which comprises contacting the diolefin in the presence of hydrogen at a temperature in the range from about 100° to 650° F. and a pressure of from about 1 to 50 atmospheres with a catalyst comprising a metal of Group IB supported on silica gel, said catalyst having been prepared by contacting said silica gel with a solution containing said metal complexed with ammonia.

2. A process for hydrogenating a diolefin to a monoolefin which comprises contacting the diolefin in the presence of hydrogen at a temperature in the range from about 100° to 650° F. and a pressure of from about 1 to 50 atmospheres with a catalyst comprising a metal of Group IB supported on silica gel, said catalyst having been prepared by contacting said silica gel with a solution containing said metal complexed with an organic amine.

3. A process for hydrogenating a diolefin to a monoolefin which comprises contacting the diolefin in the presence of hydrogen at a temperature in the range from about 100° to 650° F. and a pressure of from about 1 to 50 atmospheres with a catalyst comprising silver supported on silica gel, said catalyst having been prepared by contacting silica gel with a solution containing silver complexed with ammonia.

4. A process for hydrogenating a diolefin to a monoolefin which comprises contacting the diolefin in the presence of hydrogen at a temperature in the range from about 100° to 650° F. and a pressure of from about 1 to 50 atmospheres with a catalyst comprising silver supported on silica gel, said catalyst having been prepared by contacting silica gel with a solution containing silver complexed with an organic amine.

5. A process for hydrogenating a diolefin to a monoolefin which comprises contacting the diolefin in the presence of hydrogen at a temperature in the range from about 100° to 650° F. and a pressure of from about 1 to 50 atmospheres with a catalyst comprising copper supported on silica gel, said catalyst having been prepared by contacting silica gel with a solution containing copper complexed with ammonia.

6. The process according to claim **4** wherein the hydrogenation is effected at a temperature in the range from 100° to 650° F. and the catalyst contains from about 1 to 15% by weight silver.

References Cited by the Examiner

UNITED STATES PATENTS

2,802,889	8/57	Frevel et al.	260—677
3,051,647	8/62	White	208—255
3,076,858	2/63	Frevel et al.	260—677

ALPHONSO D. SULLIVAN, *Primary Examiner.*