

[54] **OXIDATIVE DEHYDROGENATION OF BUTANE**

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[51] Int. Cl.² **C07C 5/48**

[58] Field of Search **260/683.3, 680 E**

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

Butane may be oxidatively dehydrogenated to a mixture of 1-and 2-butenes and butadiene at high space velocities using a catalyst comprising V₂O₅, K₂SO₄, SO₃ and SiO₂.

8 Claims, No Drawings

OXIDATIVE DEHYDROGENATION OF BUTANE

BACKGROUND OF THE INVENTION

This invention relates to a process for the oxidative dehydrogenation of butane. More particularly, it relates to an improved method for the vapor phase oxidative dehydrogenation of butane to form a mixture of 1- and 2-butenes and butadiene, employing a catalyst system which permits the use of space velocities substantially higher than those previously demonstrated by prior art.

Four references exemplifying known prior art oxidative dehydrogenation methods for carrying out this process by the use of various catalysts are as follows: French Pat. No. 1,326,396 (sodium or lithium phosphomolybdates); U.S. Pat. No. 3,119,111 (lithium phosphomolybdate); British Pat. No. 943,941 (calcium nickel phosphate); and U.S. Pat. No. 3,320,331 (Al₃PO₄-supported molybdenum and vanadium). Each of these methods, while useful in the dehydrogenation of butane, is characterized by relatively low space velocities and selectivities.

SUMMARY OF THE INVENTION

It has now been found, in accordance with the present invention, that butane may effectively be oxidatively dehydrogenated to butenes and butadiene at high space velocities when there is employed a catalyst comprising a mixture of an alkali metal compound, a vanadium oxide, and sulfur dioxide, supported on an SiO₂ carrier. When thus employed, this alkali metal/V.S catalyst permits the use of gaseous hourly space velocities in the range of about 1000–20,000 hr.⁻¹, i.e. velocities which are at least 5–10 times those reported in the prior art.

DESCRIPTION OF THE INVENTION

In carrying out this process, it is desirable that the feed stream comprise substantially pure n-butane, but this is not essential. Thus, the feed stock may contain a mixture of C₄ to C₆ hydrocarbons rich in n-butane admixed with other C₄ hydrocarbons as butenes, isobutenes, isobutane, as well as pentane and like compounds derived from straight run fractions, from thermal or catalytic dehydrogenation, and/or from cracking of C₄ and higher hydrocarbons. These other materials, when present, are substantially inert to the conditions of this reaction, and thus act as inert diluents. The butane should in any event, be present in the feed stream in amounts of from about 1 to 50 wt. percent, based on the total weight of the hydrocarbons, oxygen, and inert materials, if any, in said stream.

Oxygen, either substantially pure or in the form of air, should preferably be present in stoichiometric amounts relative to the amount of butane in the feed stream, i.e. in about a 1:1 mol ratio, although ratios of 0.1:1 to 20:1 may be employed if desired. However, if the oxygen concentration is increased much beyond this latter range, competing oxidations start to take place with a resultant decrease in yield of desired product and an increase in the formation of CO₂. The oxygen is preferably introduced into the reactor by admixing it with the feed stream before it enters the reactor.

The catalyst which has been found to be uniquely effective for this process, as aforementioned, is a vanadium/alkali metal/sulfur catalyst on an SiO₂ support where the alkali metal is preferably potassium. Typical

amongst these is a catalyst having the composition, by weight of 9% V₂O₅; 29% K₂SO₄; 12% SO₃; and 50% SiO₂, wherein the catalyst has a surface area of about 40 m²/g. One such catalyst is Catalyst No. 902, obtainable from W. P. Grace & Co. It will be understood, of course, that the weight percent of the catalyst components may be varied somewhat within the skill of the art while still providing the desired dehydrogenation effect. That is to say, the percentage range of the vanadium, potassium and sulfur components of the above-described catalyst may be determined routinely by simply noting the effect of the catalyst on the space velocity and selectivity to desired end products. Space velocities in the range of about 1000 to 20,000 hrs.⁻¹, based on total gaseous feed, which provide selectivities of 50 to 100 percent are considered within the scope of this invention.

The catalyst is generally provided in the form of pellets, so that desirably it is used in the reactor in the form of a fixed bed over which the gaseous feed stream is passed. Alternatively, of course, the catalyst may be provided in the form of a fluidized bed, or other conventional arrangements known in the art which permit rapid contact of a gas and/or liquid with a particulate solid catalyst.

The reaction is conveniently carried out at temperatures of from about 450° to 650°C., and preferably from about 500° to 600°C. The gas hourly space velocity (GHSV), as described above, should be in the range of from about 1000 to 20,000 hr.⁻¹, and preferably above 10,000 hr.⁻¹. The pressure in the reactor may be any convenient, practical pressure ranging from 1 to 100 atmospheres absolute. The mol ratio of butane to oxygen, as aforesaid, should desirably be 1:1, although somewhat higher amounts of oxygen may be used if desired.

The invention will now be illustrated by the following examples.

EXAMPLE 1

A series of runs was carried out. In the first run 2.0 mls (2.0g) of catalyst was placed in a 6 × 1/4 inches stainless steel reactor and a gaseous mixture of n-butane (1%) and air (99%) was passed over the catalyst bed at 630°C and at a GHSV=8100 hr.⁻¹. The conversion was 17% while the selectivity to butenes and butadiene was 82%.

The above procedure was then repeated, varying the concentration and reaction conditions. As will be seen from the above run and those in the following table, the GHSV for the vanadium-potassium-sulfur catalyst system of the invention is at least 5–10 times greater than for known catalyst systems. The practical significance of this substantial increase is an increase in the space-time-yield or the ability to operate a smaller reactor, depending upon the desires of the operator.

TABLE I

% C ₄ Conc.	Temp. °C	GHSV hr ⁻¹	Conversion	Selectivity to Butene and Butadiene
1	610	12,000	20	66
1	550	12,000	25	65
1	500	4,050	25	75
11	550	13,680	8	90
22	550	12,000	14	75

The invention claimed is:

1. A process for the oxidative dehydrogenation of butane to form a mixture of butenes and butadiene which comprises contacting said butane with oxygen in the presence of an oxidative dehydrogenation catalyst having a composition of about 9 wt. percent V_2O_5 ; about 29 wt. percent K_2SO_4 ; about 12 wt. percent SO_3 ; and about 50 wt. percent SiO_2 , wherein the reaction is carried out at temperatures of from about 450° to 650°C and at a GHSV of from about 1000 to 20,000 hr^{-1} , and wherein the ratio of oxygen to butane is in the range of from about 1:1 to 20:1.

2. The process according to claim 1 wherein the catalyst comprises V_2O_5 , K_2SO_4 and SO_3 supported on SiO_2 , wherein said catalyst has a surface area of 40 m^2/g .

3. The process according to claim 1 wherein the oxy-

gen is supplied to the reaction in the form of air.

4. The process according to claim 1 wherein the mol ratio of oxygen to butane in the feed is about 1:1.

5. The process according to claim 1 wherein the reaction is carried out at a temperature of from about 500° to 600°C.

6. The process according to claim 1 wherein the GHSV is from 5000 to 15,000 hr^{-1} .

7. The process according to claim 1 wherein the butane is admixed with other C_4 to C_6 hydrocarbons.

8. The process according to claim 1 wherein the butane is present in the feed stream in amounts of from about 1 to 50 wt. percent, based on the total weight of the hydrocarbons, oxygen, and inerts in said stream.

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