Claims

1. Process for preparing 1,3-butadiene by heterogeneously catalysed oxidative dehydrogenation of n-butene, in which a butene mixture comprising at least 2-butene is provided,

wherein

a) the butene mixture provided is subjected to a heterogeneously catalysed isomerization to obtain an at least partly isomerized butene mixture,

b) and wherein the at least partly isomerized butene mixture is then subjected to oxidative dehydrogenation,

wherein

the isomerization is effected in such a way that 2-butene present in the butene mixture provided is isomerized to 1-butene, such that the 1-butene content in the at least partly isomerized butene mixture has increased compared to the butene mixture provided,

wherein

the isomerization catalyst comprises at least two different components, the two components having been mixed with one another or the first component having been applied to the second component, the first component is an alkaline earth metal oxide selected from the group comprising magnesium oxide, calcium oxide, strontium oxide, barium oxide, and where the proportion by weight of the alkaline earth metal oxide in the overall isomerization catalyst is between 0.5% and 20% and the second component is aluminium oxide or silicon dioxide or a mixture of aluminium oxide and silicon dioxide or an aluminosilicate

and wherein

the dehydrogenation catalyst used is a bismuth molybdate of the general formula (I):

$$(Mo_a\ Bi_b\ Fe_c\ (Co+Ni)_d\ D_e\ E_f\ F_g\ G_h\ H_i)\ O_x \qquad (I)$$

in which

D: at least one of the elements from W, P,

E: at least one of the elements from Li, K, Na, Rb, Cs, Mg, Ca, Ba, Sr,

F: at least one of the elements from Cr, Ce, Mn, V,

G: at least one of the elements from Nb, Se, Te, Sm, Gd, La, Y, Pd, Pt, Ru, Ag, Au,

H: at least one of the elements from Si, Al, Ti, Zr

and

the coefficients a to i represent rational numbers selected from the following ranges, including the specified limits:

a = 10 to 12

b= 0 to 5

c = 0.5 to 5

d = 2 to 15

e = 0 to 5

f = 0.001 to 2

g = 0 to 5

h = 0 to 1.5

i = 0 to 800

and

x is a number which is determined by the valency and frequency of the elements other than oxygen,

and in which a product mixture containing 1,3-butadiene is drawn off from the oxidative dehydrogenation and subjected to a butadiene removal, in the course of which 1,3-butadiene is separated from other constituents of the product mixture, wherein a portion of the product

mixture is recycled and blended with the butene mixture provided and/or with the at least partially isomerized butene mixture.

2. Process according to Claim 1,

wherein

the at least partly isomerized butene mixture is subjected to the oxidative dehydrogenation without prior removal of components.

3. Process according to Claim 1 or 2,

wherein

the isomerization is effected in the presence of an isomerization catalyst, and wherein the oxidative dehydrogenation is effected in the presence of a dehydrogenation catalyst, and the isomerization catalyst and dehydrogenation catalyst are not identical.

4. Process according to Claim 1,

wherein

strontium oxide as first component has been applied to aluminium oxide as second component.

5. Process according to Claim 1,

wherein

magnesium oxide as first component has been mixed with an aluminosilicate as second component.

6. Process according to any of Claims 1 to 5,

wherein

the isomerization is effected in an isomerization arrangement of the following specification:

a) the isomerization arrangement comprises a reaction zone and a regeneration zone;

b) the isomerization is effected within the reaction zone of the isomerization arrangement in the presence of isomerization catalyst disposed in the reaction zone of the isomerization arrangement;

c) there is simultaneous regeneration of isomerization catalyst disposed in the regeneration zone of the isomerization arrangement, especially by burning off deposits on the isomerization catalyst with an oxygenous gas;

d) there is continuous exchange of isomerization catalyst between the reaction zone and the regeneration zone of the isomerization arrangement.

7. Process according to any of Claims 1 to 5,

wherein

the isomerization is effected in an isomerization arrangement of the following specification:

a) the isomerization arrangement comprises two universal zones, each of which is utilizable either as reaction zone or as regeneration zone;

b) one of the two universal zones is utilized as reaction zone for isomerization, while the other universal zone is being utilized as regeneration zone for regeneration of the isomerization catalyst;

c) the isomerization is effected within the universal zone utilized as reaction zone in the presence of isomerization catalyst disposed in the reaction zone;

d) there is simultaneous regeneration of isomerization catalyst disposed in the universal zone utilized as regeneration zone, especially by burning off deposits on the isomerization catalyst with an oxygenous gas.

8. Process according to Claim 7,

wherein

the respective functions of the universal zones are switched cyclically.

9. Process according to Claim 7,

wherein

both universal zones are utilized as reaction zones in parallel until a level of deactivation is attained, and wherein then one of the two universal zones is utilized as regeneration zone, while the other universal zone continues to be utilized as reaction zone.

10. Process according to any of the preceding claims,

wherein

the butene mixture is provided in gaseous form and the isomerization and/or the oxidative dehydrogenation is conducted under the following reaction conditions:

- temperature: 250°C to 500°C, especially 300°C to 420°C
- pressure: 0.08 to 1.1 MPa, especially 0.1 to 0.8 MPa
- weight hourly space velocity (g(butenes)/g(active catalyst composition)/h): 0.1 h^{-1} to 5.0 h^{-1}, especially 0.15 h^{-1} to 3.0 h^{-1}

11. Process according to any of the preceding claims, wherein the oxidative dehydrogenation is performed in the presence of steam and oxygen,

wherein

steam and/or oxygen is added to the at least partly isomerized butene mixture.

12. Process according to any of the preceding claims,

wherein

the oxidative dehydrogenation is performed in the presence of an inert gas such as, more particularly, nitrogen and/or steam.

13. Process according to any of the preceding claims,

wherein

the butene mixture provided has a 1-butene content below the thermodynamic equilibrium concentration of 1-butene that arises from the temperatures that exist in the oxidative dehydrogenation and/or in the isomerization, especially wherein the butene mixture provided obeys the following specification:

a) the proportion by weight of hydrocarbons having four carbon atoms, based on the overall butene mixture provided, is at least 90%;

b) the total proportion by weight of n-butane and isobutane, based on the overall butene mixture provided, is 0% to 90%;

c) the total proportion by weight of isobutene, 1-butene, cis-2-butene and trans-2-butene, based on the overall butene mixture provided, is 5% to 100%;

d) the total proportion by weight of cis-2-butene and trans-2-butene, based on the butene content of the butene mixture provided, is 5% to 100%.

14. Process according to Claim 13,

wherein

the ratio of the 1-butene present in the butene mixture provided to the 2-butene present in the butene mixture provided is subject to variation over time.

15. Process according to Claim 14,

wherein

the absolute 1-butene and 2-butene contents in the butene mixture provided are subject to variation over time.