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DescriptionProcess and catalyst station for the dehydrogenation
of alkanes

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The invention relates to a process for the catalytic dehydrogenation of alkanes having a chain length of from 2 to 10 carbon atoms, in which a diluent gas is mixed into a feed containing the alkanes, the mixed stream is passed under dehydrogenating conditions over a catalyst section containing catalyst particles and the alkanes in the mixed stream are at least partially dehydrogenated and converted mainly into alkenes having the same carbon chain length as the alkanes.

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The invention also relates to a catalyst station comprising at least two reactors for the catalytic dehydrogenation of alkanes, where each reactor contains tubes which contain catalyst beds and are connected in parallel and the tubes connected in parallel are located in a furnace chamber with overhead firing.

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The preparation of propene from a hydrocarbon feed in a steam cracker is known. It is coupled in a particular ratio with ethene production from the hydrocarbon feed. However, since propene consumption is rising more quickly than ethene consumption, decoupling of propene and ethene production is required.

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Decoupling is made possible by the introduction of processes for the dehydrogenation of alkanes. Such a process is described, for example, in the publication: H. Bölt et al., "Dehydrogenation of propane/butane" in Linde Reports on Science and Technology No. 49 (1991). The endothermic dehydrogenation is carried out in a reactor of the reformer type with overhead firing. Such a reactor makes virtually isothermal operation possible. A constant conversion and product composition, as is required, in particular, in the

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fractionation section downstream of the reactor for isolating the pure products in an industrial operation, is achieved by gradually increasing the temperature of the reactor. Thus, dehydrogenation operation without a
5 decrease in the conversion and the selectivity of the reaction in the direction of the desired alkenes over the course of 6 hours can be achieved without the reactor being regenerated during this time. In this process, the desired conversion and selectivity are
10 achieved with the aid of a chromium catalyst not specified in the publication without steam dilution and usually without hydrogen dilution.

Data on conversion and selectivity are not given.

US Patent 4 902 849 discloses a process which
15 employs a catalyst containing an aluminate formed from metals of group IIA and IIB, containing metal compounds of group IVA and containing metals of group VIII of the Periodic Table of the Elements. In an example of this process, it is shown that when using a $\text{ZnO}/\text{Al}_2\text{O}_3/\text{SnO}_2/\text{Pt}$
20 catalyst, the isobutane conversion decreases from 58.2 to 50.8% and the selectivity of the reaction to isobutene increases from 84.4% to 92.0% during a running time of 6.7 hours with a high steam dilution of about 4 mol/mol. However, better selectivity and
25 conversion as well as lower steam dilution are desirable.

It is therefore an object of the invention to increase the conversion and selectivity of the dehydrogenation at low steam dilution and to make
30 possible more economical preparation of the alkene products.

This object is achieved according to the invention by a process having the features of Claim 1 and by a catalyst station having the features of Claim
35 16. Embodiments of the invention are subject-matter of dependant claims.

The process of the invention is characterized in that the diluent gas is formed by steam and hydrogen, the mixed stream is conveyed isothermally

through the catalyst section and the catalyst which promotes the dehydrogenation is formed by platinum and tin on a hydrotalcite support and is used in particulate form in the catalyst section.

5 The dilution makes it possible to set an alkane partial pressure which is lower than the process pressure and gives a favourable equilibrium for the reaction. The use of steam and hydrogen leads to long operating times with the catalyst used, since less
10 carbon is deposited on the catalyst than is the case in the prior art because most of the carbon is gasified in the reaction $C + H_2O \rightarrow CO + H_2$.

 In the feed, it is possible to use the alkanes butane and propane or mixtures thereof and as butane
15 preferably isobutane. The catalyst used according to the invention has been developed for these types of feed and is therefore particularly suitable for these.

 In the mixed stream formed by the steam, the hydrogen and the alkanes, it is possible to use,
20 depending on the alkanes used, a proportion of steam of from 0.5 to 2 mol/mol and a proportion of hydrogen of from 5 to 25 mol%. The undesirable carbon formation is then less than 0.05 percent by weight of the alkanes used.

25 To set dehydrogenation conditions, a pressure in the range from atmospheric pressure to 10 bar, preferably from atmospheric pressure to 1.3 bar, can be used in the catalyst section. Lower pressures shift the reaction equilibrium in the direction of the alkene and
30 thus increase the alkene yield. Avoidance of subatmospheric pressure enables leakages of air into the reaction space to be prevented.

 To set dehydrogenation conditions, a temperature in the range from 570 to 650°C, preferably
35 from 580 to 620°C, can be used in the catalyst section. At a high conversion, e.g. a from 40 to 60% conversion of propane to propene, only very little carbon formation occurs and long operating times without regeneration are achieved.

To set dehydrogenation conditions in the catalyst section, a space velocity of from 500 to 2000 h⁻¹, preferably from 800 to 1100 h⁻¹, can be used.

5 The dehydrogenation conditions are advantageously maintained for a running time of from 6 to 100 hours, preferably from 30 to 80 hours, without regeneration being carried out.

10 The catalyst section is best regenerated at a time before or after the running time of the dehydrogenation.

For continuous operation beyond the running time of the catalyst section, it is possible to use at least one further catalyst section, in which case a cyclic procedure is employed with always at least one
15 catalyst section being operated under dehydrogenation conditions and a further catalyst section being regenerated.

For continuous operation, it is advantageous to use a total of three reactor sections and to employ a
20 cyclic procedure in which always two catalyst sections are operated under dehydrogenation conditions and a third catalyst section is regenerated.

The catalyst section can be regenerated by burning off carbon formed during the dehydrogenation,
25 by passing a regeneration gas over the catalyst section, where the regeneration gas is formed by introduction of oxygen, for example by feeding in air or oxygen, in an amount which is increased steplessly or stepwise into steam and/or into an inert gas such as
30 nitrogen, and by, in a subsequent step, passing hydrogen or a mixture of hydrogen and alkanes over the catalyst section. Here, for example, alkanes as are in the feed are used. This regeneration procedure achieves reduction of the catalyst surface for a next
35 dehydrogenation step.

In the following, C_x represents carbon compounds having a chain length of x carbon atoms in the molecule; C_x. (or C_x.) represents molecules having x or more than x (or x or less than x) carbon atoms.

In the alkane-containing feed, it is possible to use propane which is converted mainly into propene in the catalyst section. The crude propene stream leaving the catalyst section can be compressed and
5 fractionated in a C_2/C_4 separation column to give a C_3 top product and a C_3 bottom product. The C_3 top product is subsequently fractionated by low-temperature rectification (LTR) into a C_3 fraction and a fraction containing mostly hydrogen.

10 In the conversion of propane into propene, carrying out the C_2/C_4 separation prior to the LTR results in a major part of the C_3 going into the bottom product and therefore bypassing the LTR, by which means the load on the costly LTR is significantly decreased
15 so that the latter can be made smaller.

The C_3 bottom product is advantageously rectified to give a C_4 fraction and a second C_3 fraction.

The first and second C_3 fractions can then be
20 fed to a single C_3 splitter and separated into a propene fraction and a propane fraction.

Alternatively, the C_3 bottom product can be fed to the C_3 splitter and the C_4 components can be separated from the bottom product of the C_3 splitter.

25 The propene fraction can be passed to further use as pure propene product. The propane fraction obtained can advantageously be recirculated to a point upstream of the catalyst section and used in the feed.

The catalyst station of the invention is
30 characterized in that the catalyst beds contain catalyst particles composed of platinum and tin on a hydrotalcite support.

The invention is illustrated by means of one embodiment and a figure.

35 The figure schematically shows an embodiment of the process of the invention with catalyst station 1 to 13, where the separation section 14 to 29 downstream of the catalyst station has a typical configuration for use of the process of the invention in a plant for

propene production. A diluent gas 2 containing steam and hydrogen is mixed into a propane-containing feed 1. The mixed stream 3 is passed at a temperature just under 600°C into a catalyst station having three
5 reactors 6 which contain, in the catalyst tubes 4, catalyst beds 5 containing a platinum/tin/hydrotalcite catalyst in the form of catalyst particles. The reactors 6 are equipped with an overhead-fired furnace chamber with burners 9. The mixed stream 3 is divided
10 into two streams 7 and 8 which are passed in parallel under dehydrogenation conditions through two of the three reactors 6. The heat input required, particularly in the first third of the catalyst section (in the figure, in the upper third of the catalyst bed 5 of the
15 reactor 6 near the entry point of the mixed stream 3 into the bed 5) and isothermal reaction conditions are made possible simply and sufficiently accurately by the overhead-fired furnace chamber with regulated burners 9. After the reaction and substantial conversion of the
20 propane present into propene, the streams 7 and 8 are combined to form a crude propene stream 10 which is passed into the separation section 14 to 29.

While two of the three reactors are operated under dehydrogenation conditions, a third reactor is
25 regenerated by first passing a regeneration gas formed by feeding an inert gas 11 and air 12 through the reactor 6 in order to burn off carbon formed during dehydrogenation operation and, in a subsequent step, passing a hydrogen-containing gas 13 through the
30 reactor in order to hydrogenate the surface of the catalyst particles.

The crude propene stream 10 passed into the separation section is compressed and fractionated in a C_2/C_4 separation column 14 to give a C_3 top product 15
35 and a C_3+ bottom product 16. The top product 15 is separated by stepwise condensation 17 into a C_2/C_3 fraction 18 and a fraction 19 containing mainly hydrogen. The fraction 18 is fractionated in a C_2/C_3

separation column 20 into a C₂ fraction 21 and a first C₃ fraction 22.

The C₃ bottom product 16 is fractionated in a C₃/C₄ separation column 23 into a C₄ fraction 24 and a second C₃ fraction 25. The first C₃ fraction 22 and the second C₃ fraction 25 are fed to a C₃ splitter 26 and separated into a propene product 27 and a propane fraction 28.

The fraction 19 and the fraction 21 can be combined and used as fuel gas 29. The propane fraction 28 can be passed to further use, in particular be recycled and utilised in the propane feed.

Example:

A propane dehydrogenation plant is operated using three reactors each having 50% of the plant capacity. At a dehydrogenation cycle of 75 hours, an H₂ dilution of 12 mol% and a steam dilution of 1:1 mol/mol (moles in each case based on the propane used) and operation at 1.2 bar, 590°C and a space velocity of 700 h⁻¹, the following results are achieved:

Propane conversion	> 50 percent
Propene selectivity	> 97 percent by weight
Carbon formation	< 0.05 percent by weight

As the example shows, the invention achieves the following advantages compared with the prior art in a plant for the dehydrogenation of alkanes. The steam dilution is lower than, for example, in the process of US 4 902 849. Despite this, the conversion and selectivity are higher. As a consequence, the plant throughput is smaller for a given amount of product, the entire plant can be made smaller and the lower propane input, lower consumption of utilities and lower capital costs make it more economical than a plant according to the prior art.



Claims

1. Process for the catalytic dehydrogenation of alkanes having a chain length of from 2 to 10 carbon
5 atoms, in which a diluent gas is mixed into a feed containing the alkanes, the mixed stream is passed under dehydrogenating conditions over a catalyst section containing catalyst particles and the alkanes in the mixed stream are at least partially
10 dehydrogenated and converted mainly into alkenes having the same carbon chain length as the alkanes, characterized in that the diluent gas is formed by steam and hydrogen, the mixed stream is conveyed isothermally through the catalyst section and the
15 catalyst which promotes the dehydrogenation is formed by platinum and tin on a hydrotalcite support and is used in particulate form in the catalyst section.
2. Process according to Claim 1, characterized in that the alkanes in the feed are butane or propane or
20 mixtures thereof and the butane used is preferably isobutane.
3. Process according to Claim 1 or 2, characterized in that in the mixed stream formed by the steam, the hydrogen and the alkanes, a proportion of
25 steam of from 0.5 to 2.0 mol/mol and a proportion of hydrogen of from 5 to 25 mol% are employed depending on the alkanes used.
4. Process according to any of Claims 1 to 3, characterized in that dehydrogenation conditions are
30 set in the catalyst section by using pressures in the range from atmospheric pressure to 10 bar, preferably from atmospheric pressure to 1.3 bar.
5. Process according to any of Claims 1 to 4, characterized in that dehydrogenation conditions are
35 set in the catalyst section by using a temperature in the range from 570 to 650°C, preferably from 580 to 620°C.



6. Process according to any of Claims 1 to 5, characterized in that dehydrogenation conditions are set in the catalyst section by using a space velocity of from 500 to 2000 h⁻¹, preferably from 800 to 1100 h⁻¹.
- 5 7. Process according to any of Claims 1 to 6, characterized in that the dehydrogenation conditions are maintained over a running time of from 6 to 100 hours, preferably from 30 to 80 hours.
- 10 8. Process according to Claim 7, characterized in that the catalyst section is regenerated at a time before or after the running time of the dehydrogenation.
- 15 9. Process according to Claim 8, characterized in that continuous operation beyond the running time of the catalyst section is achieved using at least one further catalyst section, in which case a cyclic procedure is employed with always at least one catalyst section being operated under dehydrogenation conditions and a further catalyst section being regenerated.
- 20 10. Process according to Claim 9, characterized in that continuous operation is achieved using a total of three reactor sections and by employing a cyclic procedure in which always two catalyst sections are operated under dehydrogenation conditions and a third
- 25 catalyst section is regenerated.
- 30 11. Process according to any of claims 8 to 10, characterized in that the catalyst section is regenerated by burning off carbon formed during the dehydrogenation, by passing a regeneration gas over the catalyst section, where the regeneration gas is formed by introduction of oxygen, for example by feeding in air or oxygen, in an amount which is increased steplessly or stepwise into steam and/or into an inert gas such as nitrogen, and by, in a subsequent step,
- 35 passing hydrogen or a mixture of hydrogen and alkanes over the catalyst section, where, for example, alkanes as in the feed are used.
12. Process according to any of claims 1 to 11, characterized in that propane is used in the alkane-



- containing feed and is converted mainly into propene in the catalyst section, the crude propene stream leaving the catalyst section is compressed, fractionated in a C_2/C_4 separation column to give a C_3 top product and a C_3 bottom product and the C_3 top product is subsequently separated by stepwise condensation into a C_2/C_3 fraction and a fraction containing mainly hydrogen and the C_2/C_3 fraction is then rectified to give a C_2 fraction and a first C_3 fraction.
13. Process according to Claim 12, characterized in that the C_3 bottom product is rectified to give a C_4 fraction a second C_3 fraction.
14. Process according to Claim 13, characterized in that the first and second C_3 fractions are fed to a C_3 splitter and separated into a propene fraction and a propane fraction.
15. Process according to Claim 12, characterized in that the C_3 bottom product is fed to the C_3 splitter and the C_4 components are separated from the bottom product of the C_3 splitter.
16. Catalyst station comprising at least two reactors for the catalytic dehydrogenation of alkanes, where each reactor contains tubes which contain catalyst beds and are connected in parallel and the tubes connected in parallel are located in a furnace chamber with overhead firing, characterized in that the catalyst beds contain catalyst particles composed of platinum and tin on a hydrotalcite support.