
Catalyst for the production of 1,3-butadiene comprising an aluminium-containing support with high favourable weight hourly space velocity

The present invention relates to a supported catalyst comprising a support and 0.1 to 10 wt.% of tantalum, calculated as Ta₂O₅ and based on the total weight of the catalyst, wherein the supported catalyst further comprises from 50 to 350 ppm of aluminium and from 1 to 50 ppm of sodium, based on the total weight of the catalyst, respectively.

5 Moreover, the invention relates to a catalyst reaction tube for the production of 1,3-butadiene comprising at least one packing of the supported catalyst as defined herein, to a reactor for the production of 1,3-butadiene comprising one or more of the catalyst reaction tubes as defined herein, and to a plant for the production of 1,3-butadiene comprising one or more of the reactors as defined herein. The invention also relates to a process for the

10 production of 1,3-butadiene as defined herein and to a process for the production of the supported catalyst as defined herein. Finally, the present invention relates to the use of the supported catalyst as defined herein for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde and to the use of aluminium in an amount in a range of from 50 to 350 ppm in a supported catalyst for the production of 1,3-butadiene from a

15 feed comprising ethanol and acetaldehyde for increasing the 1,3-butadiene productivity of the catalyst.

1,3-Butadiene is one of the most important raw materials in the synthetic rubber industry, where it is used as a monomer in the production of a wide range of synthetic polymers, such as polybutadiene rubbers, acrylonitrile-butadiene-styrene polymers, styrene-

butadiene rubbers, nitrile-butadiene rubbers, and styrene-butadiene latexes. 1,3-Butadiene is, for example, obtained as a by-product of ethylene manufacturing in naphtha steam cracking and can be isolated by extractive distillation (*Chem. Soc. Rev.*, 2014, **43**, 7917; *ChemSusChem*, 2013, **6**, 1595; *Chem. Central J.*, 2014, **8**, 53).

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The depletion of non-renewable, fossil fuels-derived resources as well as environmental considerations have recently become strong driving forces for the exploration of renewable sources of 1,3-butadiene and its precursors. Of the wide range of the available renewable sources, biomass seems to have the greatest potential in the context of use for the production of 1,3-butadiene. This strategy has two main advantages: independence from fossil fuels and reduction of CO₂ emissions (*ChemSusChem*, 2013, **6**, 1595).

The conversion of ethanol, obtainable e.g. from biomass, to 1,3-butadiene may be performed in two ways reported in the literature: as one-step process (Lebedev process) and as two-step process (Ostromislensky process).

The one-step process, reported by Lebedev in the early part of the 20th century, is carried out by direct conversion of ethanol to 1,3-butadiene, using multifunctional catalysts tuned with acid-base properties (*J. Gen. Chem.*, 1933, **3**, 698; *Chem. Ztg.*, 1936, **60**, 313).

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On the other hand, the so-called two-step process may be performed by converting, in a first step, ethanol to acetaldehyde. The aim of this first step is to feed a second step or reactor with such mixture of ethanol and acetaldehyde. In the second step, conversion of the mixture of ethanol and acetaldehyde to 1,3-butadiene over, for example, a silica-supported tantalum catalyst takes place (*Catal. Today*, 2016, **259**, 446).

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US 2018/0208522 A1 relates to a catalyst for the conversion of a feed comprising ethanol and acetaldehyde to 1,3-butadiene. The catalyst comprises at least the element tantalum, and at least one mesoporous oxide matrix that has undergone an acid wash comprising at least 90 % by weight of silica before washing, the mass of the element tantalum being in the range 0.1 % to 30 % of the mass of said mesoporous oxide matrix. The teaching of US 2018/0208522 A1 relies on acid washing of the mesoporous oxide support for increasing the selectivity of the catalyst towards 1,3-butadiene and/or the productivity of the catalyst towards 1,3-butadiene. At the end of the washing step and before impregnation of the active element(s), the catalyst contains amounts of sodium in the range of 0 to 500 ppm. Concentrations of aluminium in the catalysts and yields of 1,3-butadiene are not disclosed in US 2018/0208522 A1.

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WO 2020/126920 A1 relates to a method for producing 1,3-butadiene from ethanol, in two reaction steps, comprising a step a) of converting the ethanol into acetaldehyde and a step b) of conversion into 1,3-butadiene, the step b) simultaneously implementing a reaction step and a regeneration step in $(n+n/2)$ fixed-bed reactors, n being equal to 4 or to a multiple thereof, comprising a catalyst, said regeneration step comprising four consecutive regeneration phases, the step b) also implementing three regeneration loops.

US 2018/200694 A1 relates to a mesoporous mixed oxide catalyst that comprises silicon and at least one metal M that is selected from the group that consists of the elements of groups 4 and 5 of the periodic table and mixtures thereof, with the mass of metal M being between 0.1 and 20% of the mixed oxide mass.

WO 2022/165190 A1 relates to a method for making a supported tantalum oxide catalyst precursor or catalyst with controlled tantalum distribution and the resulting supported tantalum catalyst. In an embodiment, the method comprises selecting a tantalum precursor with appropriate reactivity with the surface hydroxyls of the solid oxide support material to give a desired tantalum distribution in the catalyst precursor or catalyst. In another embodiment, the method comprises controlling the number of surface hydroxyls available on the support material to react with the tantalum precursor by thermal methods, such as calcining, to achieve the desired tantalum distribution.

There is an ongoing need for the provision of catalysts for the production of 1,3-butadiene that have both high selectivity to 1,3-butadiene and high 1,3-butadiene productivity.

In a first aspect, the present invention relates to a supported catalyst comprising or consisting of

- (i) a support, and
- (ii) 0.1 to 10 wt.%, preferably 2 to 4 wt.%, of tantalum, calculated as Ta_2O_5 and based on the total weight of the catalyst,

wherein the supported catalyst further comprises aluminium in a range of from 50 to 350 ppm, preferably from 100 to 300 ppm, more preferably from 150 to 275 ppm, most preferably from 200 to 250 ppm, based on the total weight of the catalyst, and sodium in a range of from 1 to 50 ppm, preferably from 5 to 50 ppm, more preferably from 10 to 40 ppm, most preferably from 10 to 30 ppm, based on the total weight of the catalyst.

During the studies underlying the present invention, it was found that supported catalysts according to the invention show a lower total conversion when compared to catalysts with a lower aluminium content (less than 50 ppm) when both types of catalysts are tested at their respective favourable weight hourly space velocity (WHSV) conditions in the synthesis of 1,3-butadiene. However, it was surprisingly found that the favourable WHSV conditions of the catalysts according to the invention are at a significantly higher level compared to catalysts with a lower aluminium content. Thus, the 1,3-butadiene productivity of the catalysts according to the invention is advantageously markedly increased compared to catalysts with a lower aluminium content. Moreover, advantageously the selectivity to 1,3-butadiene increases for the catalysts according to the invention as the WHSV is increased (cf. examples, **Table 3** and **Figures 2 to 4** below).

A favourable WHSV condition as referred to herein is firstly specified by a stable selectivity of a catalyst towards 1,3-butadiene during time on stream (TOS) = 100 h. Secondly, a favourable WHSV enables the catalyst to reach the highest 1,3-butadiene productivity that satisfies the first requirement.

Sodium and aluminium levels as indicated herein in parts per million relate to the total weight of the supported catalyst including tantalum as tantalum oxide. The same applies to the tantalum levels as indicated herein in wt.%.

In one preferred embodiment, the support of the supported catalyst according to the invention comprises one or more of ordered and non-ordered porous silica supports, other porous oxide supports and mixtures thereof, preferably from ZrO₂, TiO₂, MgO, ZnO, NiO, and CeO₂.

Most preferably, the support of the supported catalyst according to the invention is a silica support, preferably an ordered or non-ordered porous silica support.

Supported catalysts are particularly advantageous, because they allow control of the concentration and dispersion of the active sites, simple preparation of the catalyst by impregnation of any form and shape of the support, and easy access of the reacting molecules to all active sites of the catalyst.

Preferably, the supported catalyst according to the invention has a BET specific surface area in a range of from 130-550 m²/g, preferably in a range of from 190 to 280 m²/g.

Preferably, the supported catalyst according to the invention has an average pore diameter in a range of from 30 to 300 Å.

Preferably, the supported catalyst according to the invention has a pore volume in a range
5 of from 0.2 to 1.5 cm³/g.

Surface area (SA) and pore volume (PV) were measured by Nitrogen Porosimetry using an Autosorb-6 Testing Unit from Quantachrome Corporation (now Anton Paar GmbH). Samples were first degassed at 350 °C for at least 4 hours on the Autosorb-6 Degassing
10 Unit. A multipoint surface area is calculated using the BET theory taking data points in the P/P₀ range 0.05 to 0.30. A pore volume measurement is recorded at P/P₀ of 0.984 on the desorption leg. Average pore diameter is calculated using the following equation assuming cylindrical pores:

$$\text{Average pore diameter } (\text{\AA}) = \frac{40000 \times PV \left(\frac{\text{cc}}{\text{g}} \right)}{SA \left(\frac{\text{m}^2}{\text{g}} \right)}$$

15 According to a preferred embodiment of the invention, the weight ratio of aluminium to sodium in the supported catalyst is in a range of from 1.0 to 350, preferably of from 1.2 to 70, more preferably of from 1.5 to 15.

Preferably, the weight ratio of aluminium to sodium in the supported catalyst according to the invention is higher than 1, i.e. preferably the supported catalyst contains more
20 aluminium than sodium.

In a second aspect, the present invention relates to a catalyst reaction tube for the production of 1,3-butadiene comprising at least one packing of the supported catalyst according to the invention and one or more packings of inert material.

25 Preferably, the inert material is selected from the group consisting of silicon carbide, inert ceramic beds, ceramic beads, extrudates, rings with a diameter of 2-7 mm, stainless steel mesh, foams, and mixtures thereof.

According to a preferred embodiment, the packings of the inert material contact and
30 separate the packings of the supported catalyst according to the invention, i.e. the reaction zones, from one another (if more than one packing of the supported catalyst is present in the catalyst reaction tube). They are preferably located at the reactant feed inlet and outlet of the reaction tube.

According to one embodiment, the catalyst reaction tube is loaded with one packing of the supported catalyst according to the invention, preferably in the centre of the catalyst reaction tube. The supported catalyst according to the invention is in contact with a packing of inert material on either side, i.e. the packings of inert material are preferably located at
5 the feed inlet and outlet of the catalyst reaction tube. According to this embodiment, the catalyst reaction tube comprises one reaction zone.

According to another embodiment, the catalyst reaction tube is loaded alternately with packings of the supported catalyst according to the invention and packings of inert material.
10 The packings of inert material are preferably located at the feed inlet and outlet of the catalyst reaction tube and contact the packings of the supported catalyst according to the invention. According to this embodiment, the catalyst reaction tube comprises more than one reaction zone.

15 In a third aspect, the present invention relates to a reactor for the production of 1,3-butadiene comprising one or more of the catalyst reaction tubes according to the invention.

In a fourth aspect, the present invention relates to a plant for the production of 1,3-butadiene comprising one or more of the reactors as defined herein, and means for regenerating the supported catalyst in said one or more reactors,
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preferably wherein the plant also comprises an acetaldehyde-producing pre-reactor with one or more reaction tubes comprising a supported or unsupported (bulk) catalyst comprising one or more of zinc, copper, silver, chromium, magnesium and nickel, preferably comprising one or more of zinc and copper.

25 Tantalum oxide, as contained in the supported catalyst according to the invention, is inactive in the oxidation of ethanol to acetaldehyde. Thus, in order to produce 1,3-butadiene with the supported catalyst according to the invention, the feed stream has to contain ethanol and acetaldehyde. This mixture of ethanol and acetaldehyde can, for instance, be
30 produced in the plant from ethanol in an acetaldehyde-producing pre-reactor comprising a supported or unsupported (bulk) catalyst as defined above, and then be fed into a reactor for the production of 1,3-butadiene comprising one or more of the catalyst reaction tubes according to the invention. Alternatively, ethanol and acetaldehyde can be obtained from commercial sources and fed directly into a reactor for the production of 1,3-butadiene
35 comprising one or more of the catalyst reaction tubes according to the invention.

In a fifth aspect, the present invention relates to a process for the production of 1,3-butadiene, the process comprising

- (i) contacting a feed comprising ethanol and acetaldehyde with the supported catalyst according to the invention to obtain a raw product comprising 1,3-butadiene.

- 5 Preferably, in the process according to the invention, the (i) contacting takes place at a temperature in a range of from 200 to 500 °C, preferably from 250 to 450 °C, more preferably from 300 to 400 °C.

- 10 In a preferred embodiment of the process according to the invention, the (i) contacting takes place at a weight hourly space velocity in a range of from 0.2 to 10 h⁻¹, preferably from 1 to 7 h⁻¹, more preferably from 2 to 6 h⁻¹, more preferably from 3 to 6 h⁻¹, more preferably from 4 to 6 h⁻¹, most preferably 4 to 5 h⁻¹.

Preferably, the (i) contacting takes place at a pressure in a range of from 0 to 10 barg, more preferably from 1 to 3 barg, most preferably from 1 to 2 barg.

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Preferably, the process according to the invention further comprises the following step(s):

- (ii) separating the raw product at least into a first portion comprising 1,3-butadiene, a second portion comprising acetaldehyde and a third portion comprising ethanol,

- 20 preferably wherein at least part of the second, of the third, or of both the second and of the third portions is recycled into the feed.

According to a preferred embodiment of the process according to the invention, the (i) contacting takes place in a continuous flow of the feed in a reactor as defined herein.

- 25 According to another preferred embodiment of the process according to the invention, the feed comprises at least 50 wt.% of ethanol, preferably comprises 60 to 75 wt.% of ethanol, based on the total weight of the feed.

According to another preferred embodiment of the process according to the invention, the feed comprises at least 15 wt.% of acetaldehyde, preferably comprises 20 to 35 wt.% of acetaldehyde, based on the total weight of the feed.

According to another preferred embodiment of the process according to the invention, the molar ratio of ethanol to acetaldehyde in the feed is in a range of from 1 to 7, preferably of from 1.5 to 5, more preferably of from 1.7 to 4, most preferably of from 2.0 to 3.0.

In a sixth aspect, the present invention relates to a process for the production of the supported catalyst according to the invention comprising or consisting of the following steps:

- (i) impregnation of the support with aluminium and sodium levels defined by the formulas below based on the weight of the catalyst support, with a solution of a tantalum precursor, to form a supported tantalum catalyst precursor,
 - wherein the lower limit is defined by: $\text{Support [M]}_{\text{LL}} = \text{Catalyst [M]}_{\text{LL}} / (1 - \text{Catalyst [Ta}_2\text{O}_5\text{]wt.\%})$, with $M = \text{Na or Al}$; where $\text{Catalyst [Na]}_{\text{LL}} = 1 \text{ ppm}$ and $\text{Catalyst [Al]}_{\text{LL}} = 50 \text{ ppm}$; and
 - the upper limit is defined by: $\text{Support [M]}_{\text{UL}} = \text{Catalyst [M]}_{\text{UL}} / (1 - \text{Catalyst [Ta}_2\text{O}_5\text{]wt.\%})$, with $M = \text{Na or Al}$; where $\text{Catalyst [Na]}_{\text{UL}} = 50 \text{ ppm}$ and $\text{Catalyst [Al]}_{\text{UL}} = 350 \text{ ppm}$;
- (ii) drying the supported tantalum catalyst precursor, and
- (iii) calcining the dried supported tantalum catalyst precursor, to form a supported tantalum catalyst.

In above formulae, $\text{Support [M]}_{\text{LL}}$ designates the lower limit of the concentration (wt./wt.) of metals M (M being sodium or aluminium, respectively) in the support to be used and to be impregnated in step (i), which is dependent on

- a. $\text{Catalyst [M]}_{\text{LL}}$, the lower limit of the concentration (wt./wt.) of metals M (M being sodium or aluminium, respectively) in the supported catalyst according to the invention to be ultimately obtained in step (iii), and
- b. $\text{Catalyst [Ta}_2\text{O}_5\text{]wt.\%}$, the concentration (wt./wt.) of Ta_2O_5 in the supported catalyst according to the invention to be ultimately obtained in step (iii).

Likewise, in above formulae, Support $[M]_{UL}$ designates the upper limit of the concentration (wt./wt.) of metals M (M being sodium or aluminium, respectively) in the support to be used and to be impregnated in step (i), which is dependent on

5 a. Catalyst $[M]_{UL}$, the upper limit of the concentration (wt./wt.) of metals M (M being sodium or aluminium, respectively) in the supported catalyst according to the invention to be ultimately obtained in step (iii), and

10 b. Catalyst $[Ta_2O_5]_{wt.\%}$, the concentration (wt./wt.) of Ta_2O_5 in the supported catalyst according to the invention to be ultimately obtained in step (iii).

15 Preferred embodiments in terms of sodium and aluminium contents of the supported catalyst according to the first aspect of the present invention correspond to preferred embodiments regarding Catalyst $[M]_{LL}$ and Catalyst $[M]_{UL}$ regarding of the sixth aspect of the invention.

20 In one preferred embodiment, the support impregnated in step (i) of the process according to the invention comprises one or more of ordered and non-ordered porous silica, other porous oxides and mixtures thereof, preferably from ZrO_2 , TiO_2 , MgO , ZnO , NiO , and CeO_2 .

Preferably, the support impregnated in step (i) of the process according to the invention is a silica support, preferably an ordered or non-ordered porous silica support.

25 According to a preferred embodiment of the process for the production of the supported catalyst according to the invention, the supported catalyst is a silica supported catalyst and the method comprises or consists of:

- (i) reacting an aqueous silicate, preferably sodium silicate, solution with an acid, to form a hydrosol,
- 30 (ii) dispersion, preferably by means of spraying, more preferably by means of spraying into air and breaking into droplets, and gelation of the hydrosol, to form hydrogel beads,
- (iii) one or more optional additional steps of (pre-)aging, acidification, washing and pH adjustment,

- a. aging of the hydrogel beads at temperature T1,
- b. acidification of the aged hydrogel beads,
- c. washing, preferably with water that is deionized and acidified to pH 3-4, of the acidified aged hydrogel beads,
- 5 d. adjusting the pH of the washed hydrogel beads obtained in step (c), preferably to a pH in a range of about 8-10,
- (iv) aging of the hydrogel beads at temperature T2, with $T2 > T1$ (if applicable, e.g., if one of the optional steps in (iii) are used),
- (v) acidification of the aged hydrogel beads (obtained in step (iv)),
- 10 (vi) washing, preferably with water that is deionized and acidified to pH 3-4, of the acidified aged hydrogel beads (obtained in step (v)),
- (vii) optionally adjusting the pH of the washed hydrogel beads obtained in step (vi), preferably to a pH in a range of about 3 to 10, most preferably to a pH of about 9,
- (viii) drying the washed hydrogel beads obtained in step (vi) or (vii) to obtain a silica support, preferably by using an oven,
- 15 (ix) optionally, sieving of the silica support obtained in step (viii) (to collect the desired particle size fraction),
- (x) impregnation of the silica support obtained in step (viii) or (ix) with a solution of a tantalum precursor, to form a supported tantalum catalyst precursor, preferably wherein the tantalum precursor is tantalum ethoxide, most preferably wherein the tantalum ethoxide precursor is stabilized with 2,4-pentanedione and/or dissolved in a suitable organic solvent such as isopropanol,
- 20 (xi) drying the supported tantalum catalyst precursor, preferably by heating at atmospheric pressure or under vacuum, and

(xii) calcining the dried supported tantalum catalyst precursor, preferably at a temperature of about 400 to 600 °C for about 2 to 5 hours, to form a supported tantalum catalyst.

As used herein, a "supported tantalum catalyst precursor" refers to an intermediate product, e.g., before calcination. In contrast, a "supported tantalum catalyst" is the product after calcination.

Preferably, temperature T1 in the process according to the invention is in a range of from 20 to 50 °C.

Preferably, temperature T2 in the process according to the invention is in a range of from 40 to 100 °C.

Preferred embodiments of a certain aspect of the present invention (cf. aspects one to ten above) correspond to or can be derived from preferred embodiments of the other aspects of the invention (as defined above), respectively, as long as technically sensible.

In a seventh aspect, the present invention relates to the use of the supported catalyst according to the invention for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde, preferably for increasing the 1,3-butadiene productivity.

In an eighth aspect, the present invention relates to the use of aluminium in an amount in a range of from 50 to 350 ppm, preferably from 100 to 300 ppm, more preferably from 150 to 275 ppm, most preferably from 200 to 250 ppm, based on the total weight of the catalyst, in a supported catalyst for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde, the catalyst comprising or consisting of

- a support,
- 1 to 50 ppm, preferably 5 to 50 ppm, more preferably 10 to 40 ppm, most preferably from 10 to 30 ppm, of sodium, based on the total weight of the catalyst, and
- 0.1 to 10 wt.%, preferably 2 to 4 wt.%, of tantalum, calculated as Ta₂O₅ and based on the total weight of the catalyst,

for increasing the 1,3-butadiene productivity of the catalyst.

In a ninth aspect, the present invention relates to the use of sodium in an amount in a range of from 1 to 50 ppm, preferably from 5 to 50 ppm, more preferably from 10 to 40 ppm, most preferably from 10 to 30 ppm, based on the total weight of the catalyst, in a supported catalyst for the production of 1,3-butadiene from a feed comprising ethanol and
5 acetaldehyde, the catalyst comprising or consisting of

- a support,
- 50 to 350 ppm, preferably 100 to 300 ppm, more preferably 150 to 275 ppm, most preferably 200 to 250 ppm, of aluminium, based on the total weight of the catalyst, and
- 10 - 0.1 to 10 wt.%, preferably 2 to 4 wt.%, of tantalum, calculated as Ta₂O₅ and based on the total weight of the catalyst,

for increasing the 1,3-butadiene productivity of the catalyst.

In a tenth aspect, the present invention relates to the use of sodium in an amount in a range of from 1 to 50 ppm, preferably from 5 to 50 ppm, more preferably from 10 to 40 ppm, most
15 preferably from 10 to 30 ppm, and of aluminium in an amount in a range of from 50 to 350 ppm, preferably from 100 to 300 ppm, more preferably from 150 to 275 ppm, most preferably from 200 to 250 ppm, based on the total weight of the catalyst respectively, in a supported catalyst for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde, the catalyst comprising or consisting of

- 20 - a support,
- 0.1 to 10 wt.%, preferably 2 to 4 wt.%, of tantalum, calculated as Ta₂O₅ and based on the total weight of the catalyst,

for increasing the 1,3-butadiene productivity of the catalyst.

Examples:

25 **1. Silica support preparation**

The following is a description of the general steps used for making the silica support according to an embodiment of the present disclosure. A flow chart showing the general

steps used in making silica support according to an embodiment of the present disclosure is provided in **Figure 1**. A more detailed description of the silica support and methods of making it are found in co-pending application number U.S. Patent Application No.: 16/804,610, which is herein incorporated by reference.

- 5 In one embodiment, a dilute sodium silicate solution of 3.3 weight ratio $\text{SiO}_2:\text{Na}_2\text{O}$ was first reacted with dilute sulfuric acid, to form a hydrosol having the following composition: 12 wt.% SiO_2 and $\text{H}_2\text{SO}_4:\text{Na}_2\text{O}$ in a molar ratio of 0.8. As a result, the resulting hydrosol was basic. In one embodiment, the sodium silicate solution contained approximately 250 ppm aluminium on SiO_2 weight basis. In one embodiment, a higher purity silicate with low
10 aluminium (< 10 ppm on SiO_2 weight basis) was used to make silica with lower aluminium content.

- The hydrosol was then sprayed into air, where it broke into droplets and solidified into beads having a diameter of several millimeters before it was caught in a solution such as water or a solution that buffers the pH of the beads/solution system at a basic pH of about 9 (such
15 as aqueous solution of ammonium sulfate, sodium bicarbonate, etc.). Higher aging temperature and/or longer aging times reduces the silica surface area. Generally, for hydrogel caught in ammonium sulfate solution to achieve a surface area of about 300 m^2/g , aging is conducted at 70 °C at a pH of about 9 for about 16 hours.

- Acid was then added to lower the pH to about 2. The hydrogel beads were then washed
20 with water that was acidified to a pH about 3 to reduce sodium levels. The aged and washed hydrogel beads contain about 15-18 % SiO_2 . Once washed, the pH of the beads was increased to about 9 using ammonium hydroxide solution. The beads were then dried using an oven. Finally, the beads were sieved to get the desired particle size fraction. Note that pH adjustment before drying is optional, and beads are typically dried from pH 3-9.

- 25 In one embodiment, the described process can be modified to optionally include multiple aging steps at increasing temperatures with each aging step followed by acidification and washing steps to get the desired combination of surface area and sodium levels. In one embodiment, optionally, washing can be done before the aging step.

- Following the procedure outlined above, one can obtain a silica gel bead with a surface
30 area of about 230-300 m^2/g , a pore volume of about 0.95-1.05 cm^3/g , aluminium < 500 ppm (depending on silicate purity and/or the process and conditions used to carry out the washing and aging steps), and sodium < 1000 ppm (depending on extent of washing in

combination with multiple aging steps). In some cases, the silica hydrogel containing low amounts of aluminium and/or sodium (on dry basis) were contacted with a solution of aluminium sulfate and/or sodium carbonate respectively before drying to adjust aluminium and/or sodium to desired levels.

5 2. Catalyst preparation

In all cases the silica gel beads with size 2-5 mm were pre-dried to a loss of drying (LOD) < 0.5 wt.%, measured at 120 °C, before use. The following is a general description of making the catalyst on a basis of using 100 g silica support on dry basis. Broadly, the tantalum precursor was added to the silica *via* the incipient wetness impregnation method.

- 10 For every 100 g (dry basis) of silica gel support, a stabilized tantalum precursor solution was made by mixing approximately 5-6 g of tantalum precursor, such as 5.7 g tantalum ethoxide with 2-3 g, such as 2.8 g of 2,4-pentanedione (acetyl acetone). In general, 8.5 g of the stabilized tantalum precursor solution was dissolved in 65-76 g isopropanol, which was then added on to the pre-dried silica gel beads. The amount of isopropanol was
- 15 adjusted based on the support pore volume, so that the solution was contained only in the silica pores, and there was no free solution outside the pores. Impregnation took around 15-40 minutes. The impregnated silica gel was kept in a sealed container for at least 1 hour before the solvent was evaporated by heating at atmospheric pressure or under vacuum. The dried material was then calcined up to 550 °C for 4 hours in air to give the finished
- 20 catalyst with approximately 3.0 wt.% Ta₂O₅. In one embodiment, Catalyst A was made using this preparation method.

Preparation of Catalyst B:

- Silica gel beads with size 2-5 mm were pre-dried to a loss of drying (LOD) < 0.5 wt.%, measured at 120 °C, before use. For 100 g (dry basis) of silica gel support, a stabilized
- 25 tantalum precursor solution was made by mixing 5.7 g tantalum ethoxide with 2.8 g of 2,4-pentanedione (acetyl acetone). In general, 8.5 g of the stabilized tantalum precursor solution was dissolved in 70 g isopropanol, which was then added on to the pre-dried silica gel beads. Impregnation took around 15-40 minutes. The impregnated silica gel was kept in a sealed container for at least 1 hour before the solvent was evaporated by heating at
- 30 atmospheric pressure. The dried material was then calcined up to 550 °C for 4 hours in air to give the finished catalyst with 3.3 wt.% Ta₂O₅, 17 ppm Na and 225 ppm Al.

The Na and Al can be assumed to be present in the support since no substantial quantities of Na or Al are present in the Ta-ethoxide, acetyl acetone or isopropanol. The amount of Na or Al in the support and catalyst is then related by the formula:

5 $\text{Support [M]} = \text{Catalyst [M]} / (1 - \text{Catalyst [Ta}_2\text{O}_5\text{]wt.\%})$, with M = Na or Al

Consequently, the Na and Al in the support are calculated to be 17.6 ppm and 232 ppm respectively.

10 Data related to the catalysts synthesized according to the above procedures are summarized in **Table 1** below.

Sample Type	Catalyst A	Catalyst B
Ta [wt%]	2.56	2.71
Ta ₂ O ₅ [wt%]	3.1	3.3
Na [ppm]	31	17
Al [ppm]	6	225
BET specific surface area [m ² /g]	252	253
Pore volume [cm ³ /g]	0.95	1.02
Average pore diameter [Å]	151	162

Table 1: Data on Catalysts A and B

15 **3. Sodium and aluminium analysis method**

The levels of sodium and aluminium in the catalyst compositions were measured by Atomic Absorption Spectroscopy (AA) using a Perkin-Elmer PinAAcleTM 900F Spectrometer and Inductively Coupled Plasma ("ICP") Spectroscopy using a Perkin Elmer Optima 8300 ICP-OES spectrometer, respectively. Samples of catalyst were digested with hydrofluoric acid (HF). The resulting silicon tetrafluoride (SiF₄) was fumed away and the residue was analyzed for sodium and aluminium. Sodium and aluminium levels are reported as the parts per million of the catalyst after drying at 120 °C. The sodium and aluminium amounts of the

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support and the tantalum starting material, respectively, can be determined accordingly if desired.

4. Tantalum analysis method

The levels of tantalum in the catalyst compositions were measured by Inductively Coupled Plasma ("ICP") Spectroscopy using a Perkin Elmer Optima 8300 ICP-OES spectrometer. Samples of catalyst were digested with hydrofluoric acid (HF). The resulting silicon tetrafluoride (SiF₄) was fumed away and the residue was analyzed for tantalum. Results are reported on dried weight basis of the catalyst calcined at 500 to 550 °C.

The physico-chemical properties of the catalysts synthesized according to the above procedure are summarized in **Table 2** below.

Catalyst	BET specific surface area [m ² /g]	Average pore diameter [Å]	Ta ₂ O ₅ content [wt. %]	Ta content [wt. %]	Al content [ppm]	Na content [ppm]
A	252	151	3.1	2.6	6	31
B	253	162	3.3	2.7	225	17

Table 2: Physico-chemical properties of the catalysts

5. Catalytic tests

40 grams of the catalysts synthesized according to the above procedure were placed into a respective continuous flow-operated stainless steel reactor. The reactor had initially been heated to 350 °C, at a nitrogen flow rate of 500 ml/min. (Nitrogen was used only when heating the reactor, whereas the reaction was carried out without nitrogen flow, but solely with the indicated organic feed.) The reaction was then carried out using 94 wt.% aqueous ethanol mixed with acetaldehyde at a mass ratio of 2.5:1 as a feed (the mass portion of 2.5 for the 94 wt.% aqueous ethanol relates to the combined weight of water and ethanol), at a pressure of 1.8 barg and with a WHSV as indicated below (cf. e.g. **Table 3**). The composition of the effluent was regularly monitored by an online gas chromatograph equipped with a flame-ionization detector coupled with a mass spectrometer (GC/MS).

Catalysts lose their activity for the production of 1,3-butadiene during the operation and require regeneration. Catalyst regeneration was carried out after 100 hours (h) time on stream (TOS) *in situ* in the stainless steel reactor, in the following four stages.

1. Desorption and removal of organic vapors

Organic vapors were removed by purging with a stream of nitrogen (gas hourly space velocity (GHSV) = 300 h⁻¹) at 350 °C for 5 hours.

2. Preliminary combustion of carbon deposits

5 Deposits were burnt in a stream of air diluted by steam (GHSV = 300 h⁻¹) for 15 hours. The oxygen content in the regeneration mixture (air/steam) was gradually increased from 1 to 6 vol.%, so that the temperature in the reactor would not exceed 400 °C.

3. Combustion of carbon deposits

10 The temperature of the reactor was increased to 520 °C. Deposits were finally burnt in a stream of air diluted by nitrogen (GHSV= 300 h⁻¹) for 20 hours. The oxygen content in the regeneration mixture (air/nitrogen) was 6 vol.%.

4. Cooling down

The reactor was cooled down to 350 °C, in a nitrogen flow (GHSV= 300 h⁻¹).

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Total conversion, selectivity, yield, and productivity were calculated as shown below (EtOH = ethanol; AcH = acetaldehyde):

$$\text{Total Conversion} = \frac{\text{moles of converted EtOH and AcH}}{\text{moles of EtOH and AcH in the feed}} \cdot 100$$

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$$\text{Selectivity} = \frac{C \text{ moles in 1,3-butadiene}}{C \text{ moles in all products}} \cdot 100$$

$$\text{Yield} = \frac{\text{Total Conversion} \cdot \text{Selectivity}}{100}$$

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$$\text{Productivity} = \frac{\text{mass flow rate of 1,3-butadiene}}{\text{mass of catalyst}}$$

The average results of the catalytic tests of the fresh (non-regenerated) catalysts are summarized in **Table 3** below. Catalyst **B** according to the invention shows a lower total conversion when compared to catalyst **A** when both catalysts are tested at their respective
 30 favourable WHSV conditions (cf. column "WHSV" in **Table 3**), however, it was found that its favourable WHSV conditions are at a significantly higher level compared to catalyst **A**. Thus, the 1,3-butadiene productivity of the catalyst is surprisingly markedly increased for catalyst **B** according to the invention, as compared to catalyst **A** (cf. also **Figure 2**, which shows that, for catalyst **B**, both 1,3-butadiene productivity and selectivity to 1,3-butadiene
 35 increase as WHSV is increased from 2 h⁻¹ to 5 h⁻¹).

Catalyst	WHSV [h ⁻¹]	Total Conversion [%]	Selectivity to 1,3-Butadiene [%]	Selectivity to C6+ [%]	Yield of 1,3-Butadiene [%]	1,3-Butadiene productivity [g _{1,3-BD} /(g _{cat} ·h)]
A	5	26	70	10	18.2	0.59
A	2.3(*)	48	72	10	34.6	0.48
B	5	33	75	7	24.8	0.76

Table 3: Results of the catalytic tests (average results for fresh catalysts with a TOS = 100 h); g - grams; h - hour; 1,3-BD - 1,3-butadiene; cat - catalyst

- 5 The impact of the impurity content of the fresh catalysts is further depicted over the course of 100 hours TOS in **Figure 3**. Again, catalyst **B** according to the invention is compared to catalyst **A** in the catalytic tests as described above. Catalyst **A** was tested both at its favourable WHSV of 2.3 h⁻¹ (*) and at a WHSV of 5 h⁻¹, and catalyst **B** was tested at a WHSV of 5 h⁻¹. As shown in **Figure 3**, the selectivity to 1,3-butadiene is higher for catalyst
- 10 **B** at a WHSV of 5 h⁻¹ than for catalyst **A** at both a WHSV of 2.3 h⁻¹ and 5 h⁻¹. Moreover, lower selectivity to heavy compounds (C6+ = side products containing 6 or more carbon atoms) as side-products leads to a more stable selectivity to 1,3-butadiene during time on stream (TOS) for catalyst **B**.
- 15 **Figure 4** further shows the performance of catalysts **A** and **B** over the course of 100 hours TOS after five regeneration cycles, respectively. Again, catalyst **A** was operated at its favourable WHSV of 2.3 h⁻¹ (*) and catalyst **B** was operated at its favourable WHSV of 5 h⁻¹. As can be taken from **Figure 4**, the selectivity to 1,3-butadiene is higher during the first couple of hours for catalyst **A**, but it decreases slowly with time on stream (TOS).
- 20 Catalyst **B**, even though it shows lower selectivity to 1,3-butadiene in the beginning of this experiment, advantageously stabilizes at the levels reached by the catalyst **A** and shows better stability and higher selectivity to 1,3-butadiene in the last 50 hours on stream. Again, a lower selectivity to heavy compounds (C6+) as side-products is observed for catalyst **B** according to the invention through the entire course of the experiment.

Claims

1. A supported catalyst comprising
 - (i) a support, and
 - (ii) 0.1 to 10 wt.% of tantalum, calculated as Ta_2O_5 and based on the total weight of the catalyst,
- wherein the supported catalyst further comprises aluminium in a range of from 50 to 350 ppm, based on the total weight of the catalyst, and sodium in a range of from 1 to 50 ppm, based on the total weight of the catalyst.
2. The supported catalyst according to claim 1, wherein the support comprises one or more of ordered and non-ordered porous silica supports, other porous oxide supports and mixtures thereof, preferably from ZrO_2 , TiO_2 , MgO , ZnO , NiO , and CeO_2 .
 3. The supported catalyst according to claim 1 or 2, wherein the supported catalyst has a BET specific surface area in a range of from 130-550 m^2/g , preferably in a range of from 190 to 280 m^2/g .
 4. The supported catalyst according to any of the preceding claims, wherein the weight ratio of aluminium to sodium is in a range of from 1.0 to 350, preferably of from 1.2 to 70.
 5. A catalyst reaction tube for the production of 1,3-butadiene comprising at least one packing of the supported catalyst as defined in any of claims 1 to 4 and one or more packings of inert material.
 6. A reactor for the production of 1,3-butadiene comprising one or more of the catalyst reaction tubes as defined in claim 5.
 7. A plant for the production of 1,3-butadiene comprising one or more of the reactors as defined in claim 6, and means for regenerating the supported catalyst in said one or more reactors,

preferably wherein the plant also comprises an acetaldehyde-producing pre-reactor with one or more reaction tubes comprising a supported or unsupported (bulk) catalyst comprising one or more of zinc, copper, silver, chromium, magnesium and nickel.

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8. A process for the production of 1,3-butadiene, the process comprising
- (i) contacting a feed comprising ethanol and acetaldehyde with the supported catalyst as defined in any of the claims 1 to 4 to obtain a raw product comprising 1,3-butadiene.

- 10 9. The process according to claim 8, wherein the (i) contacting takes place at a temperature in a range of from 200 to 500 °C, preferably from 250 to 450 °C, more preferably from 300 to 400 °C.

10. The process according to claim 8 or 9, wherein the (i) contacting takes place at a weight hourly space velocity in a range of from 0.2 to 10 h⁻¹, preferably from 1 to 7 h⁻¹, most preferably 4 to 5 h⁻¹.

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11. The process according to any of the claims 8 to 10, wherein the (i) contacting takes place at a pressure in a range of from 0 to 10 barg, preferably from 1 to 3 barg.

- 20 12. The process according to any of the claims 8 to 11, further comprising

- (ii) separating the raw product at least into a first portion comprising 1,3-butadiene, a second portion comprising acetaldehyde and a third portion comprising ethanol,

preferably wherein at least part of the second, of the third, or of both the second and of the third portions is recycled into the feed.

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13. The process of any of the claims 8 to 12, wherein the (i) contacting takes place in a continuous flow of the feed in a reactor as defined in claim 6.

14. A process for the production of the supported catalyst as defined in any of the claims 1 to 4 comprising or consisting of the following steps:

- (i) impregnation of the support with aluminium and sodium levels defined by the formulas below based on the weight of the catalyst support, with a solution of a tantalum precursor, to form a supported tantalum catalyst precursor,
- wherein the lower limit is defined by: $\text{Support [M]}_{\text{LL}} = \text{Catalyst [M]}_{\text{LL}} / (1 - \text{Catalyst [Ta}_2\text{O}_5\text{]wt.\%})$, with $M = \text{Na or Al}$; where $\text{Catalyst [Na]}_{\text{LL}} = 1 \text{ ppm}$ and $\text{Catalyst [Al]}_{\text{LL}} = 50 \text{ ppm}$; and
- the upper limit is defined by: $\text{Support [M]}_{\text{UL}} = \text{Catalyst [M]}_{\text{UL}} / (1 - \text{Catalyst [Ta}_2\text{O}_5\text{]wt.\%})$, with $M = \text{Na or Al}$; where $\text{Catalyst [Na]}_{\text{UL}} = 50 \text{ ppm}$ and $\text{Catalyst [Al]}_{\text{UL}} = 350 \text{ ppm}$;
- (ii) drying the supported tantalum catalyst precursor, and
- (iii) calcining the dried supported tantalum catalyst precursor, to form a supported tantalum catalyst.
15. The process for the production of the supported catalyst as defined in claim 14, wherein the supported catalyst is a silica supported catalyst and the method comprises or consists of:
- (i) reacting an aqueous silicate, preferably sodium silicate, solution with an acid, to form a hydrosol,
- (ii) dispersion and gelation of the hydrosol, to form hydrogel beads,
- (iii) one or more optional additional steps of (pre-)aging, acidification, washing and pH adjustment,
- a. aging of the hydrogel beads at temperature T_1 ,
- b. acidification of the aged hydrogel beads,
- c. washing, preferably with water that is deionized and acidified to pH 3-4, of the acidified aged hydrogel beads,

- d. adjusting the pH of the washed hydrogel beads obtained in step (c), preferably to a pH in a range of about 8-10,
- (iv) aging of the hydrogel beads at temperature T2, with $T2 > T1$,
- (v) acidification of the aged hydrogel beads,
- 5 (vi) washing, preferably with water that is deionized and acidified to pH 3-4, of the acidified aged hydrogel beads,
- (vii) optionally adjusting the pH of the washed hydrogel beads obtained in step (vi),
- (viii) drying preferably 2 to 4 wt.%, the washed hydrogel beads obtained in step (vi) or (vii) to obtain a silica support,
- 10 (ix) optionally, sieving of the silica support obtained in step (viii),
- (x) impregnation of the silica support obtained in step (viii) or (ix) with a solution of a tantalum precursor, to form a supported tantalum catalyst precursor,
- (xi) drying the supported tantalum catalyst precursor, and
- (xii) calcining the dried supported tantalum catalyst precursor, to form a supported
15 tantalum catalyst.
16. Use of the supported catalyst as defined in any of the claims 1 to 4 for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde, preferably for increasing the 1,3-butadiene productivity.
17. Use of aluminium in an amount in a range of from 50 to 350 ppm, based on the total
20 weight of the catalyst, in a supported catalyst for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde, the catalyst comprising
- a support,
 - 1 to 50 ppm of sodium, based on the total weight of the catalyst,

- 0.1 to 10 wt.% of tantalum, calculated as Ta_2O_5 and based on the total weight of the catalyst,

for increasing the 1,3-butadiene productivity of the catalyst.