Supported oxide catalyst comprising tantalum, aluminium and sodium having high selectivity in the production of 1,3-butadiene

The present invention relates to a supported oxide catalyst comprising specific amounts of tantalum, aluminium and sodium. Moreover, the invention relates to a catalyst reaction tube for the production of 1,3-butadiene comprising at least one packing of the supported oxide catalyst as defined herein, to a fixed bed 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 fixed bed reactors as defined herein. The invention also relates to a process for the production of 1,3-butadiene as defined herein. Finally, the present invention relates to the use of the supported oxide catalyst as defined herein for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde; and to the use of sodium in a supported oxide catalyst for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde, for increasing selectivity of the supported oxide catalyst to 1,3-butadiene.

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).

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 CO_2 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).

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).

WO2022165190A1 relates to a method for making a supported tantalum oxide catalyst precursor or catalyst with controlled Ta distribution and the resulting supported Ta catalyst. In an embodiment, the method comprises selecting a Ta precursor with appropriate reactivity with the surface hydroxyls of the solid oxide support material to give a desired Ta distribution in the catalyst precursor or catalyst. In an embodiment the method comprises controlling the number of surface hydroxyls available on the support material to react with the Ta precursor by thermal methods, such as calcining, to achieve the desired Ta distribution.

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.

Thus, there is an ongoing need for supported oxide catalysts for the production of 1,3-butadiene that show high activity and are able to provide high selectivity to 1,3-butadiene.

In a first aspect, the present invention relates to a supported oxide catalyst comprising

(i) tantalum in an amount in a range of from 0.1 to 10 wt.%, calculated as Ta_2O_5 and based on the total weight of the supported oxide catalyst,

(ii) aluminium in an amount in a range of from 8 to 46 ppm, based on the total weight of the supported oxide catalyst, and

(iii) sodium in an amount in a range of 125 ppm or less, based on the total weight of the supported oxide catalyst.

During the studies underlying the present invention, it was found that tantalum-containing supported oxide catalysts according to the invention, containing defined levels of sodium and aluminium as defined in the first aspect, give high selectivity to 1,3-butadiene.

Sodium and aluminium levels as indicated herein in parts per million relate to the total weight of the supported oxide catalyst.

In one preferred embodiment, (ii) the supported oxide catalyst comprises aluminium in an amount in a range of from 10 ppm to 45 ppm, preferably in a range of from 12 ppm to 40 ppm, more preferably in a range of from 15 ppm to 35 ppm, based on the total weight of the supported oxide catalyst, respectively.

In a further preferred embodiment, the supported oxide catalyst comprises sodium in an amount in a range of from 1 ppm to 125 ppm, preferably in a range of from 30 ppm to 80 ppm, more preferably in a range of from 45 ppm to 60 ppm, based on the total weight of the supported oxide catalyst, respectively.

Supported oxide catalysts are 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.

In one preferred embodiment, the supported oxide catalyst 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,

Preferably, the supported oxide catalyst comprises one or more of ordered and non-ordered porous silica supports.

Most preferably, the supported oxide catalyst comprises non-ordered porous silica.

Preferably, the supported oxide catalyst according to the first aspect has a BET specific surface area in a range of from 130 to 550 m^2/g, preferably in a range of from 190 to 280 m^2/g.

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

Preferably, the supported oxide catalyst according to the invention has a pore volume in a range of from 0.2 to 1.5 cm^3/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 Unit. A multipoint surface area is calculated using the BET theory and taking data points in the P/P_0 range 0.05 to 0.30. A pore volume measurement is recorded at P/P_0 of 0.984 on the desorption leg. Average pore diameter is calculated using the following equation assuming cylindrical pores:

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

According to a preferred embodiment of the first aspect of the invention, the weight ratio of aluminium to sodium in the supported oxide catalyst is in a range of from 1.5 to 20, preferably in a range of from 1.8 to 10, more preferably in a range of from 2.0 to 8, in particular in a range of from 2.5 to 5, in particular in a range of from 3.0 to 4.0.

In one preferred embodiment, the supported oxide catalyst comprises (iv) calcium in an amount in a range of from 1 to 100 ppm, based on the total weight of the supported oxide catalyst.

In one preferred embodiment, the supported oxide catalyst comprises (v) iron in an amount in a range of from 1 to 50 ppm, each based on the total weight of the supported oxide catalyst.

In one preferred embodiment, the supported oxide catalyst comprises (vi) titanium in an amount in a range of from 1 to 150 ppm, based on the total weight of the supported oxide catalyst.

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 oxide catalyst according to the first aspect, and one or more packings of inert material.

In one embodiment, the inert material is selected from the group consisting of silicon carbide, inert ceramic beds, ceramic beads, extrudates, rings with a diameter in a range of 2 to 7 mm, stainless steel mesh, foams, and mixtures thereof.

According to a preferred embodiment, the packings of the inert material contact and separate the packings of the supported oxide catalyst according to the invention, i.e. the reaction zones, from one another (if more than one packing of the supported oxide 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 oxide catalyst according to the invention, preferably in the centre of the catalyst reaction tube. The supported oxide catalyst according to the first aspectis in contact with a packing of inert material on either side, i.e. the packings of inert material are preferably located at 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 alternatingly with packings of the supported oxide catalyst according to the first aspect and packings of inert material. 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 oxide catalyst

according to the first aspect. According to this embodiment, the catalyst reaction tube comprises more than one reaction zone.

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

In a fourth aspect, the present invention relates to a plant for the production of 1,3-butadiene comprising one or more of the fixed bed reactors as per the third aspect, and means for regenerating the supported oxide catalyst in said one or more fixed bed reactors.

According to one embodiment, 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, and nickel, preferably comprising one or more of zinc and copper.

Tantalum oxide, as contained in the supported oxide catalyst according to the invention, is by itself inactive in the oxidation of ethanol to acetaldehyde. Thus, in order to produce 1,3-butadiene with the supported oxide catalyst according to the invention, the feed stream has to contain ethanol and acetaldehyde. This mixture of ethanol and acetaldehyde can, for instance, be 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 fixed bed 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 fixed bed reactor for the production of 1,3-butadiene 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

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

Preferably, in the process according to the fifth aspect, the (1) 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.

In a preferred embodiment of the process according to the fifth aspect, the (1) contacting takes place at a weight hourly space velocity in a range of from 0.2 to 10 h^{-1}, preferably from 0.3 to 5 h^{-1}, more preferably from 0.5 to 3 h^{-1}.

Preferably, the (1) 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.

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

(2) 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.

According to a preferred embodiment of the process according to the fifth aspect of the invention, the (1) contacting takes place in a continuous flow of the feed in a fixed bed reactor as per the third aspect.

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.

Further disclosed is a process for the production of the supported oxide 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: Support $[M]_{LL}$ = Catalyst $[M]_{LL}$ /(1-Catalyst $[Ta_2O_5]$wt.%), with M = Na or Al; where Catalyst $[Na]_{LL}$ = 0 ppm and Catalyst $[Al]_{LL}$ = 46 ppm; and

the upper limit is defined by: Support $[M]_{UL}$ = Catalyst $[M]_{UL}$ /(1-Catalyst $[Ta_2O_5]$wt.%), with M = Na or Al; where Catalyst $[Na]_{UL}$ = 125 ppm and Catalyst $[Al]_{UL}$ = 46 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, Support $[M]_{LL}$ 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. Catalyst $[M]_{LL}$, the lower limit of the concentration (wt./wt.) of metals M (M being sodium or aluminium, respectively) in the supported oxide catalyst according to the invention to be ultimately obtained in step (iii), and

b. Catalyst $[Ta_2O_5]$wt.%, the concentration (wt./wt.) of Ta_2O_5 in the supported oxide 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

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

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

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

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.

According to a preferred embodiment of the process for the production of the supported oxide catalyst, the supported oxide catalyst is a silica supported oxide 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, 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,

d. adjusting the pH of the washed hydrogel beads obtained in step (c), preferably to a pH in a range of about 8 to 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)),

(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,

(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,

(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 “tantalum-containing supported oxide 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.

In a sixth aspect, the present invention relates to the use of the supported oxide catalyst according to the first aspect of the invention for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde.

In a seventh aspect, the present invention relates to the use of of aluminium in an amount in a range of from 8 ppm to 46 ppm, preferably in a range of from 10 ppm to 45 ppm, more

preferably in a range of from 12 ppm to 40 ppm, even more preferably in a range of from 15 ppm to 35 ppm,

in a supported oxide catalyst for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde, the catalyst further comprising

- 125 ppm or less of sodium, based on the total weight of the supported oxide catalyst,

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

for increasing selectivity of the supported oxide catalyst to 1,3-butadiene.

Preferred embodiments of a certain aspect of the present invention (cf. aspects one to seven 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.

Examples:

1. <u>Silica support preparation</u>

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 general but more detailed description of the silica support and methods of making it are found in US20210269562A1, which is herein incorporated by reference.

In one embodiment, a dilute sodium silicate solution of 3.3 weight ratio SiO_2:Na_2O was reacted with dilute sulfuric acid, to form a hydrosol having the following composition: 12 wt.% SiO_2 and H_2SO_4:Na_2O in a molar ratio of 0.8. As a result, the resulting hydrosol was basic. Sodium silicate with low aluminium (< 50 ppm on SiO_2 weight basis) was used to ensure low Al content in the resultant silica gel.

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 an aqueous ammonium sulfate buffer solution such that the pH of the beads/solution system was about 9. The

beads were then aged at 45°C. Acid was then added to lower the pH to about 2. The hydrogel beads were then washed with water that was acidified to a pH of about 3. Additional ammonium sulfate was then added back to the beads, and pH of the bead/solution system adjusted to about 9 using aq. ammonia. The hydrogel beads were aged again at 90°C, followed by acidification to pH 2 and then washing with acidified water of pH about 3. The two-step aging/acidification/washing was followed to ensure the desired combination of surface area and 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.

Following the procedure outlined above, one can obtain a silica gel bead with a surface area of about 230-300 m^2/g, a pore volume of about 0.95-1.05 cm^3/g, aluminium < 50 ppm (depending on silicate purity and/or the process and conditions used to carry out the washing and aging steps), and sodium < 125 ppm.

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 supported oxide 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.

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 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 supported oxide catalyst with approximately 3.0 wt.% Ta_2O_5.

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 used.

3. Sodium and aluminium analysis method

The levels of sodium and aluminium in the supported oxide catalyst 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 supported oxide catalyst were digested with hydrofluoric acid (HF). The resulting silicon tetrafluoride (SiF_4) 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 supported oxide catalyst after drying at 120 °C. The sodium and aluminium amounts of the support and the tantalum starting material, respectively, can be determined accordingly if desired.

4. Tantalum analysis method

The levels of tantalum in the supported oxide catalyst were measured by Inductively Coupled Plasma ("ICP") Spectroscopy using a Perkin Elmer Optima 8300 ICP-OES spectrometer. Samples of supported oxide catalyst were digested with hydrofluoric acid (HF). The resulting silicon tetrafluoride (SiF_4) was fumed away and the residue was analyzed for tantalum. Results are reported on dried weight basis of the supported oxide catalyst calcined at 500 to 550 ºC.

Catalyst Properties	Unit	Catalyst	
		A (invention)	B (comparative)
Tantalum as Ta	wt.%[1]	2.6	2.7
Sodium as Na	ppm[1]	58	17
Aluminum as Al	ppm[1]	17	225
Surface Area	m^2/g[1]	255	253
Pore Volume	cm^3/g[1]	1.0	1.0
Average Pore Diameter	Å	159	162
Calcium as Ca	ppm[1]	19	10
Iron as Fe	ppm[1]	12	76
Titanium as Ti	ppm[1]	116	97

Table 1: Physico-chemical properties of the supported oxide catalysts synthesized according to the above procedure. [1] Dry basis.

5. Catalytic tests

50 grams of the supported oxide catalysts synthesized according to the above procedure were placed into a continuous flow-operated stainless steel fixed bed 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 feed (the mass portion of 2.5 for the 94 wt.% aqueous ethanol relates to the combined weight of water and ethanol), with a weight hourly space velocity (WHSV) of 2.0 h^{-1} and at a pressure of 1.8 barg. 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).

Supported oxide catalysts lose their activity for the production of 1,3-butadiene during operation and require regeneration. Supported oxide catalyst regeneration may be carried out *in situ* in the stainless steel reactor, in the following four stages:

1. Desorption and removal of organic vapors
   Organic vapors are 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
   Deposits are 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) is gradually increased from 1 to 6 vol.%, so that the temperature in the reactor would not exceed 400 °C.

3. Combustion of carbon deposits
   The temperature of the reactor is increased to 520 °C. Deposits are 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) is 6 vol.%.

4. Cooling down
   The reactor is cooled down to 350 °C, in a nitrogen flow (GHSV = 300 h^{-1}).

Results from testing the catalyst performance were calculated as follows and are indicated in **Table 2** below (EtOH - ethanol; AcH - acetaldehyde):

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

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

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

Average for 10 h TOS	Catalyst	
	A (invention)	B (comparative)
Total Conversion [%]	62	58
Selectivity to 1,3-BD [%]	74	69
Selectivity to ethylene [%]	4	9
Yield 1,3-BD [%]	46	40

Table 2: Comparison of activity and selectivity of fresh supported oxide catalysts at **WHSV = 2.0 h^{-1}**. Further process conditions: T = 350(±2) °C, p = 1.8 barg, 94 wt.% EtOH:AcH = 2.5:1 wt./wt.; 1,3-BD = 1,3-butadiene. TOS = Time On Stream.

It is apparent from Table 2 that the catalyst according to the invention performs favourably both in terms of total conversion and selectivity to 1,3-butadiene. This results in higher yield to 1,3-butadiene, as compared to the use of the comparative catalyst.

Claims

1. A supported oxide catalyst comprising

(i) tantalum in an amount in a range of from 0.1 to 10 wt.%, calculated as Ta_2O_5 and based on the total weight of the supported oxide catalyst,

(ii) aluminium in an amount in a range of from 8 to 46 ppm, based on the total weight of the supported oxide catalyst, and

(iii) sodium in an amount in a range of 125 ppm or less, based on the total weight of the supported oxide catalyst.

2. The supported oxide catalyst according to claim 1, wherein

(ii) the supported oxide catalyst comprises aluminium in an amount in a range of from 10 ppm to 45 ppm, preferably in a range of from 12 ppm to 40 ppm, more preferably in a range of from 15 ppm to 35 ppm, based on the total weight of the supported oxide catalyst, respectively;

and/or

(iii) the supported oxide catalyst comprises sodium in an amount in a range of from 1 ppm to 125 ppm, preferably in a range of from 30 ppm to 80 ppm, more preferably in a range of from 45 ppm to 60 ppm, based on the total weight of the supported oxide catalyst, respectively.

3. The supported oxide catalyst according to any one of claims 1 or 2, wherein the supported oxide catalyst 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,

preferably wherein the supported oxide catalyst comprises one or more of ordered and non-ordered porous silica supports,

in particular wherein the supported oxide catalyst comprises non-ordered porous silica.

4. The supported oxide catalyst according to any one of the preceding claims 1 to 3, wherein the supported oxide catalyst has a BET specific surface area in a range of from 130 m^2/g to 550 m^2/g, preferably in a range of from 190 m^2/g to 280 m^2/g.

5. The supported oxide catalyst according to any one of the preceding claims 1 to 4, wherein the weight ratio of aluminium to sodium is in a range of from 1.5 to 20, preferably in a range of from 1.8 to 10, more preferably in a range of from 2.0 to 8, in particular in a range of from 2.5 to 5, in particular in a range of from 3.0 to 4.0.

6. The supported oxide catalyst according to any one of the preceding claims 1 to 5, comprising

(iv) calcium in an amount in a range of from 1 to 100 ppm,
(v) iron in an amount in a range of from 1 to 50 ppm,
and/or
(vi) titanium in an amount in a range of from 1 to 150 ppm,

each based on the total weight of the supported oxide catalyst.

7. A catalyst reaction tube for the production of 1,3-butadiene comprising at least one packing of the supported oxide catalyst as defined in any one of claims 1 to 6, and one or more packings of inert material.

8. A fixed bed reactor for the production of 1,3-butadiene comprising one or more of the catalyst reaction tubes as defined in claim 7.

9. A plant for the production of 1,3-butadiene comprising x) one or more of the fixed bed reactors as defined in claim 8, and y) means for regenerating the supported oxide catalyst in said one or more fixed bed reactors,

preferably wherein the plant also z) 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.

10. A process for the production of 1,3-butadiene, the process comprising

(1) contacting a feed comprising ethanol and acetaldehyde with the supported oxide catalyst as defined in any one of claims 1 to 6, to obtain a raw product comprising 1,3-butadiene.

11. The process according to claim 10, wherein

- the (1) 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;

and/or

- the (1) contacting takes place at a weight hourly space velocity in a range of from 0.2 to 10 h^{-1}, preferably from 0.3 to 5 h^{-1}, most preferably 0.5 to 3 h^{-1}.

12. The process according to any one of claims 10 to 11, wherein the (1) contacting takes place at a pressure in a range of from 0 to 10 barg, preferably from 1 to 3 barg, most preferably from 1 to 2 barg.

13. The process according to any one of claims 10 to 12, further comprising the step

(2) 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 portion or at least part of the third portion is recycled into the feed,

or

- at least parts of both the second portion and the third portion are recycled into the feed.

14. The process of any one of claims 10 to 13, wherein the (1) contacting takes place in a continuous flow of the feed in a fixed bed reactor as defined in claim 8.

15. Use of the supported oxide catalyst as defined in any one of claims 1 to 6 for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde.

16. Use of aluminium in an amount in a range of from 8 ppm to 46 ppm, preferably in a range of from 10 ppm to 45 ppm, more preferably in a range of from 12 ppm to 40 ppm, even more preferably in a range of from 15 ppm to 35 ppm,

in a supported oxide catalyst for the production of 1,3-butadiene from a feed comprising ethanol and acetaldehyde, the catalyst further comprising

- 125 ppm or less of sodium, based on the total weight of the supported oxide catalyst,

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

for increasing selectivity of the supported oxide catalyst to 1,3-butadiene.