

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

03 March 2022 (03.03.2022)



(10) International Publication Number

WO 2022/043323 A1

(51) International Patent Classification:

B01J 23/22 (2006.01)

C07C 51/215 (2006.01)

B01J 27/198 (2006.01)

MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/EP2021/073382

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

(22) International Filing Date:

24 August 2021 (24.08.2021)

Published:

— with international search report (Art. 21(3))

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

20192543.5

25 August 2020 (25.08.2020)

EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,

(54) Title: MIXED OXIDE COMPRISING NB, V, AND P SUITABLE AS CATALYST FOR PARTIAL OXIDATION OF HYDROCARBONS

(57) Abstract: A mixed oxide comprising Nb, V, P, and O, exhibiting a molar ratio of Nb to the sum of Nb and V, Nb:(Nb+V), of equal to or greater than 0.091:1, comprising a crystalline NbOPO₄ phase, and comprising a crystalline alpha(II) VOPO₄ phase in an amount in the range of from equal to or greater than 50 weight-%, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, determined as disclosed herein.



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Mixed oxide comprising Nb, V, and P suitable as catalyst for partial oxidation of hydrocarbons

TECHNICAL FIELD

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The present invention relates to a novel type of a mixed oxide suitable as catalyst or catalyst component, in particular for the partial oxidation of hydrocarbons, and preferably for short chained hydrocarbons. The mixed oxide according to the present invention particularly comprises Nb, V, and P, and may be used as such, or supported on a support material. Further, a process for preparing such a mixed oxide is disclosed.

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DETAILED DESCRIPTION

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The industrial synthesis of oxygenates as for example maleic anhydride or acrolein, is of high interest since these compounds represent essential building blocks in organic chemistry. Typically, short-chain hydrocarbons are converted in a catalytic reaction, in particular by selective partial oxidation, to the respective oxygenates, whereby the activation of the C-H bond can be seen as a crucial step. As a benchmark catalyst vanadyl pyrophosphate (VPP) can be mentioned, which generally represents the only industrially relevant catalyst for the partial oxidation of n-butane to maleic anhydride. For its synthesis, vanadyl phosphate ($\text{VO}(\text{HPO}_4) \cdot 0.5 \text{H}_2\text{O}$) is converted into vanadyl pyrophosphate $(\text{VO})_2(\text{P}_2\text{O}_7)$. With the said catalyst it is possible to achieve conversion rates of about 60 to 65 %, especially when applying optimized process conditions. Another known catalyst is represented by $\text{WOPO}_4\text{-VOPO}_4$ comprising an $\alpha(\text{II})$ VOPO_4 crystal phase.

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With respect to its possible crystal phases, seven polymorphs are known for anhydrous VOPO_4 , denoted α_I , α_{II} , β , γ , δ , ω , and ϵ . According to the present invention, the designation $\alpha(\text{I})$ is equally used to α_I , the designation $\alpha(\text{II})$ is equally used to α_{II} , and so on.

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Said polymorphs are known and can be found in the Inorganic Crystal Structure Database (ICSD). Further, a review on the polymorph is given by E. Bordes, Catal. Today 1 (1987) 499–526. In particular, Tachez et al. published their results on $\alpha(\text{I})$ VOPO_4 (ICSD 108983) in J. Solid. State Chem. 1981, 40, 280, and on $\alpha(\text{II})$ VOPO_4 (ICSD 77598) in J. Solid State Chem. 1981, 40, 280. Gopal et al. published their results on beta VOPO_4 (ICSD 9413) in J. Solid State Chem. 1972, 5, 432, Dornhaus et al. on gamma VOPO_4 (ICSD 415213) in Private Comm. 2005, 1, 1, Girgsdies et al. on delta VOPO_4 (ICSD 420073) in Solid State. Sci. 2009, 77, 1258, and on epsilon VOPO_4 (ICSD 415924) in Solid State. Sci. 2006, 8, 807, Amoros et al. on omega VOPO_4 (ICSD 167245) in J. Phys. Chem. Solids 2001, 62, 1393.

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By now, however, above mentioned catalyst could not compete with VPP with respect to its activity. Other catalysts are known from the prior art, which particularly include Nb as further component.

Mastuura et al. disclose in Catalysis Today a study on the promotional effect of niobium phosphate for vanadyl pyrophosphate catalyst on selective oxidation of butane to maleic anhydride. Disclosed are compounds having the empirical formula $V_{1-x}Nb_xOPO_4$, wherein x is in the range of from 0 to 0.3. The catalyst having a ratio of Nb:(Nb + V) of 0.2 showed the best test results with respect to the oxidation of butane.

P. G. Pries de Oliveira et al. disclose in Catalysis Today a modification of vanadium phosphorus oxides used for n-butane oxidation to maleic anhydride by interaction with niobium phosphate. In particular, mixtures of vanadium phosphorus oxides with niobium phosphate are disclosed.

WO 2005/025742 A1 relates to a process for the preparation of a modified vanadium/phosphorus mixed oxide catalyst for the partial oxidation of n-butane to maleic anhydride. Disclosed therein are catalysts comprising vanadyl pyrophosphate as main component, and niobium as a promoter element in an amount corresponding to an atomic ratio of vanadium to niobium in the range of from 250 : 1 to 60 : 1, respectively a ratio Nb:(Nb + V) of from 0.0040:1 to 0.0164:1.

Y. Wang et al. disclose in Industrial and Engineering Chemistry Research a study on a Nb-doped vanadium phosphorus oxide catalyst for the aldol condensation of acetic acid with formaldehyde to acrylic acid. It is disclosed that when the molar ratio Nb:V is 0.06:1, respectively a molar ratio Nb:(Nb + V) of 0.0566, the catalyst surface has the greatest acidity, and the selectivity and yield of acrylic acid are maximized.

A. Caldarelli et al. disclose in Catalysis Science and Technology an investigation on surface reactivity of a Nb-doped vanadyl pyrophosphate catalysts by reactivity experiments and in situ Raman spectroscopy. Catalysts have been prepared with different V:Nb atomic ratios, e. g. equal to 150:1, 80:1, and 46:1, respectively Nb:(Nb + V) of 0.0066:1, 0.0123:1 and 0.0213:1, whereby the P:V molar ratio was equal to 11:10.

Thus, it was an object of the present invention to provide a mixed oxide suitable as alternative catalyst or catalyst component to vanadyl pyrophosphate, which show catalytic activity in the partial oxidation, in particular in the selective partial oxidation, of hydrocarbons. Further, it was an object of the present invention to provide a mixed oxide, which shows catalytic activity in the partial oxidation of hydrocarbons and is suitable for industrial use, in particular considering its economical requirements, especially as regards an improved reaction efficiency. Further, it was an object of the present invention to provide a process for preparation of such a mixed oxide. In particular, it was an object to provide an improved process for preparation of a mixed oxide, which can be easily applied and/or does not suffer from any known disadvantage.

To this effect, different mixed oxides comprising Nb, V, P, and O have been prepared and tested with respect to their catalytic activity in the partial oxidation of n-butane and propane. It was surprisingly found that the prepared mixed oxides show a high flexibility with respect to their structure and their composition.

Further, it was surprisingly found that the mixed oxides of the present invention comprising Nb, V, P, and O can be easily prepared. In this regard, it is preferred to prepare the mixed oxides via solution combustion synthesis, which allows for a high, but rather uncontrolled, energy input in a system. This preparation method permits short process durations. Further, the preparation of the mixed oxides of the present invention is possible, including hydrothermal reaction conditions applied on a reaction mixture. In addition to that, the mixed oxide can be prepared by dry impregnation of suitable precursors on an appropriate support material, resulting in a composition wherein the mixed oxide is then supported on a support material.

Surprisingly, the mixed oxides of the present invention comprising Nb, V, P, and O show activity as catalyst in the partial oxidation, in particular in the selective partial oxidation, of hydrocarbons. As hydrocarbons, in particular alkanes and alkenes can be used, as for example n-butane, propylene and propane. Other hydrocarbons may equally be used.

Thus, it was surprisingly found that the mixed oxides of the present invention are effective with respect to the partial oxidation of a hydrocarbon. In particular, it was surprisingly found that the mixed oxides of the present invention show a high activity and selectivity in the partial oxidation of hydrocarbons, especially with respect to the conversion of propane to propylene, or of n-butane to maleic anhydride. In this regard, a good selectivity towards propylene and maleic anhydride, respectively, has been found, in particular in connection with good conversion rates. Thus, it has been surprisingly been found that a mixed oxide being comparatively niobium-rich shows a comparatively high selectivity towards propylene as well as towards maleic anhydride.

Therefore, the present invention relates to a mixed oxide comprising Nb, V, P, and O, exhibiting a molar ratio of Nb to the sum of Nb and V, Nb:(Nb+V), of equal to or greater than 0.091:1, comprising a crystalline NbOPO₄ phase, and comprising a crystalline alpha(II) VOPO₄ phase in an amount in the range of from equal to or greater than 50 weight-%, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, preferably determined as described in Reference Example 1, wherein the crystalline NbOPO₄ phase and/or the crystalline alpha(II) VOPO₄ phase and the respective amounts thereof are more preferably determined as described in Reference Example 1.

It is preferred that the crystalline alpha(II) VOPO₄ phase comprised in the mixed oxide exhibits an X-ray diffraction pattern comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
110	19.33 – 21.16
111	28.77 – 29.68
200	27.60 – 29.99

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1,
preferably comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
001	19.83 – 21.84
110	19.43 – 21.06
101	24.79 – 25.98
111	28.87 – 29.58
200	27.70 – 29.89

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1,

more preferably comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
001	19.93 – 21.74
110	19.53 – 20.96
101	24.89 – 25.88
111	28.97 – 29.48
200	27.80 – 29.79

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1.

It is preferred that the mixed oxide further comprises amorphous VOPO_4 in a total amount in the range of from 0 to 1 weight-%, preferably in the range of from 0 to 0.5 weight-%, more preferably in the range of from 0 to 0.1 weight-%, based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 , preferably determined via electron microscopy with coupled elemental analysis, more preferably by high-resolution transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (HRTEM coupled with EDX).

It is preferred that the mixed oxide further comprises one or more crystalline VOPO_4 phases other than the crystalline $\alpha(\text{II})$ VOPO_4 phase in a total amount in the range of from 0 to 1 weight-%, preferably in the range of from 0 to 0.5 weight-%, more preferably in the range of from 0 to 0.1 weight-%, based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 .

It is preferred that the mixed oxide exhibits a molar ratio of Nb to the sum of V, Nb, and P, $\text{Nb}:(\text{V}+\text{Nb}+\text{P})$, of equal to or greater than 0.1:1, preferably of equal to or greater than 0.14:1, more preferably in the range of from 0.167:1 to 0.495:1, more preferably in the range of from 0.1875:1 to 0.49:1, more preferably in the range of from 0.24:1 to 0.48:1, more preferably in the range of from 0.3:1 to 0.469:1, more preferably in the range of from 0.33:1 to 0.45:1, more preferably in the range of from 0.344:1 to 0.45:1.

It is preferred that the mixed oxide comprises the crystalline $\alpha(\text{II})$ VOPO_4 phase in an amount in the range of from 50 to 88.8 weight-%, preferably in the range of from 60 to 84 weight-%, more preferably in the range of from 70 to 80 weight-%, based on the sum of the

weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 , preferably determined as described in Reference Example 1.

It is preferred that the mixed oxide exhibits a molar ratio of V to the sum of V, Nb, and P, $\text{V}:(\text{V}+\text{Nb}+\text{P})$, in the range of from 0.005:1 to 0.495:1, preferably in the range of from 0.01:1 to 0.35:1, more preferably in the range of from 0.015:1 to 0.25:1, more preferably in the range of from 0.025:1 to 0.2:1, more preferably in the range of from 0.045:1 to 0.155:1.

It is preferred that the mixed oxide exhibits a molar ratio of P to the sum of V, Nb, and P, $\text{P}:(\text{V}+\text{Nb}+\text{P})$, in the range of from 0.40:1 to 0.60:1, more preferably in the range of from 0.45:1 to 0.55:1, more preferably in the range of from 0.49:1 to 0.51:1.

It is preferred that from 90 to 100 weight-%, preferably from 95 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.9 to 100 weight-%, of the mixed oxide consist of V, Nb, P, O, and H.

It is preferred that the mixed oxide comprises from 0 to 10 weight-%, preferably from 0 to 5 weight-%, more preferably from 0 to 1 weight-%, more preferably from 0 to 0.1 weight-%, more preferably from 0 to 0.01 weight-%, more preferably from 0 to 0.001 weight-%, of a crystalline $(\text{VO})_2\text{P}_2\text{O}_7$ (vanadyl pyrophosphate) phase, based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 , preferably determined as described in Reference Example 1.

In the case where the mixed oxide comprises a crystalline $(\text{VO})_2\text{P}_2\text{O}_7$ (vanadyl pyrophosphate) phase, it is preferred that the crystalline $(\text{VO})_2\text{P}_2\text{O}_7$ (vanadyl pyrophosphate) phase exhibits an X-ray diffraction pattern comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle $2\theta/\text{°}$ [Cu K(α 1)]
012	13.91 – 14.31
111	15.44 – 15.84
020	18.29 – 18.69
200	22.77 – 23.17
024	28.23 – 28.63
032	29.74 – 30.14
016	33.51 – 33.91
224	36.66 – 37.06
036	43.03 – 43.43
400	46.73 – 47.13

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1,

preferably comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle $2\theta/\text{°}$ [Cu K(α 1)]
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012	14.01 – 14.21
111	15.54 – 15.74
020	18.39 – 18.59
200	22.87 – 23.07
024	28.33 – 28.53
032	29.84 – 30.04
016	33.61 – 33.81
224	36.76 – 36.96
036	43.13 – 43.33
400	46.83 – 47.03

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1.

5 It is preferred that the mixed oxide is essentially free of a crystalline $(VO)_2P_2O_7$ (vanadyl pyrophosphate) phase.

It is preferred that the mixed oxide comprises, preferably consisting of, a solid solution.

10 In the case where the mixed oxide comprises, preferably consisting of, a solid solution, it is preferred according to a first alternative that the solvent is the crystalline $\alpha(II)$ $VOPO_4$ phase, calculated as $VOPO_4$, if the amount of said crystalline phase in the mixed oxide is higher than the amount of the crystalline α $NbOPO_4$ phase, calculated as $NbOPO_4$, in the mixed oxide, based on the sum of the weight of Nb calculated as $NbOPO_4$ and of V calculated as $VOPO_4$, wherein the amount of a crystalline phase is preferably determined as described in Reference
15 Example 1.

In the case where the mixed oxide comprises, preferably consisting of, a solid solution, it is preferred according to a second alternative that the solute is the crystalline $\alpha(II)$ $VOPO_4$ phase if the amount of said crystalline phase in the mixed oxide is smaller than the amount of the crystalline α $NbOPO_4$ phase in the mixed oxide, based on the sum of the weight of Nb calculated as $NbOPO_4$ and of V calculated as $VOPO_4$, wherein the amount of a crystalline phase is preferably determined as described in Reference Example 1.
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25 It is preferred that the mixed oxide comprises the crystalline $NbOPO_4$ phase in an amount of less than 50 weight-%, preferably in the range of from 16 to 40 weight-%, more preferably in the range of from 20 to 30 weight-%, based on the sum of the weight of Nb calculated as $NbOPO_4$ and of V calculated as $VOPO_4$, preferably determined as described in Reference Example 1.

30 It is preferred that the crystalline $NbOPO_4$ phase comprised in the mixed oxide comprises from 75 to 100 weight-%, preferably from 85 to 100 weight-%, more preferably from 90 to 100 weight-%, more preferably from 95 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.9 to 100 weight-%, of a crystalline α $NbOPO_4$ phase, based on the sum

of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, preferably determined as described in Reference Example 1.

- It is preferred that the crystalline NbOPO₄ phase comprised in the mixed oxide comprises from 0 to 25 weight-%, preferably from 0.1 to 15 weight-%, more preferably from 1 to 10 weight-%, more preferably from 4 to 5 weight-%, of a crystalline beta NbOPO₄ phase, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, preferably determined as described in Reference Example 1.
- 10 In the case where the crystalline NbOPO₄ phase comprised in the mixed oxide comprises a crystalline beta NbOPO₄ phase as described herein, it is preferred that the crystalline beta NbOPO₄ phase exhibits an X-ray diffraction pattern comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
110	15.30 – 15.70
200	15.50 – 15.90
210	20.46 – 20.86
011	21.29 – 21.69
111	22.71 – 23.11
211	26.52 – 26.92
310	27.04 – 27.44
121	32.64 – 33.04
002	33.70 – 34.10
401	35.86 – 36.26

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1,

- 15 preferably comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
110	15.40 – 15.60
200	15.60 – 15.80
210	20.56 – 20.76
011	21.39 – 21.59
111	22.81 – 23.01
211	26.62 – 26.82
310	27.14 – 27.34
121	32.74 – 32.94
002	33.80 – 34.00
401	35.96 – 36.16

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1.

It is preferred that the mixed oxide comprises a crystalline phase of a metaphosphate anion, a polyphosphate anion, or a mixture of two or more thereof, preferably of a diphosphate anion, a triphosphate anion, a tetrphosphate anion, a trimetaphosphate anion, a tetrametaphosphate anion, or a mixture of two or more thereof, and one or more of NbO^{3+} and VO^{3+} .

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It is preferred that the mixed oxide comprises the crystalline phase of the metaphosphate anion, the polyphosphate, or the mixture of two or more thereof, preferably of the diphosphate anion, the triphosphate anion, the tetrphosphate anion, the trimetaphosphate anion, the tetrametaphosphate anion, or the mixture of two or more thereof, and of the one or more of NbO^{3+} and VO^{3+} , in an amount in the range of from 0 to 2 weight-%, preferably in the range of from 0.01 to 1 weight-%, more preferably in the range of from 0.1 to 0.5 weight-%, based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 .

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It is preferred that the mixed oxide further comprises one or more of an element E other than Nb, V, P, and O, preferably selected from groups 1 to 15 of the periodic system of elements including lanthanides, more preferably selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Sm, Ti, Zr, Hf, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, and Bi, more preferably selected from the group consisting of Ti, Zr, Hf, Ta, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Ge, Sn, Pb, Sb, and Bi, more preferably selected from the group consisting of Ta, Mo, W, Fe, Co, Ni, and Sb.

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In the case where the mixed oxide further comprises one or more of an element E other than Nb, V, P, and O as described herein, it is preferred that the mixed oxide comprises the one or more of an element E in an amount in the range of from 0.1 to 10 weight-%, preferably in the range of from 1 to 7.5 weight-%, more preferably in the range of from 2.5 to 5 weight-%, calculated as element and based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 .

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It is preferred that the mixed oxide is a tempered mixed oxide, wherein the tempering was carried out by subjecting the mixed oxide to a heat treatment in a gas atmosphere, said gas atmosphere preferably comprising, more preferably consisting of, air, dry air, nitrogen, argon, or a mixture of two or more thereof, wherein the temperature of the gas atmosphere during the heat treatment is in the range of from 350 to 750 °C, preferably in the range of from 400 to 700 °C, and wherein the heat treatment was preferably carried out for a duration in the range of from 6 h to 5 d, preferably in the range of from 12 h to 4 d.

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It is preferred that the mixed oxide was not subjected to a heat treatment as defined in embodiment (24).

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It is preferred that the mixed oxide has a BET specific surface area in the range of from 1 to 100 m^2/g , preferably in the range of from 3 to 75 m^2/g , more preferably in the range of from 10 to 50 m^2/g , preferably determined according to Reference Example 3.

It is preferred that the mixed oxide is supported on a support material.

5 In the case where the mixed oxide is supported on a support material, it is preferred that the support material is selected from the group consisting of silica, alumina, silica-alumina, titania, silica-titania, alumina-titania, silica-alumina-titania, and a mixture of two or more thereof, where-
in the support material preferably comprises, more preferably consists of, silica.

10 Further in the case where the mixed oxide is supported on a support material, it is preferred that the support material has a BET specific surface area in the range of from 1 to 300 m²/g, preferably in the range of from 3 to 300 m²/g, more preferably in the range of from 10 to 200 m²/g preferably determined according to Reference Example 3.

15 Further, the present invention relates to a process for preparing a mixed oxide comprising Nb, V, P, and O, preferably for preparing a mixed oxide according to any one of the embodiments disclosed herein, the process comprising

- (a) providing a reaction mixture comprising a source of Nb, a source of V, a source of P, wa-
ter, and optionally an oxidizing agent;
- (b) optionally drying the reaction mixture obtained in (a) in a gas atmosphere having a tem-
20 perature in the range of from 50 to 100 °C, obtaining a dried reaction mixture;
- (c) subjecting the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) to a thermal treatment in a gas atmosphere, obtaining a precursor of the mixed oxide;
- (d) subjecting the precursor of the mixed oxide obtained in (c) to tempering, said tempering
25 comprising, preferably consisting of, subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature of at least 300 °C, ob-
taining the mixed oxide.

30 It is preferred that the source of Nb comprised in the reaction mixture according to (a) comprises, preferably consists of, one or more of ammonium niobate(V) oxalate, niobium monoxide, niobium dioxide, niobium pentoxide, lithium niobate, potassium niobate, niobium(III) chloride, niobium(V) chloride, niobium carbide, niobium oxychloride, and niobium ethoxide, wherein the source of Nb preferably comprises, more preferably consists of, ammonium niobate(V) oxalate, preferably ammonium niobate(V) oxalate hydrate.

35 It is preferred that the source of V comprised in the reaction mixture according to (a) comprises, preferably consists of, one or more of an ammonium orthovanadate, an ammonium divanadate, an ammonium metavanadate, and an ammonium polyvanadate, wherein the source of V preferably comprises, more preferably consists of, an ammonium metavanadate.

40 It is preferred that the source of P comprised in the reaction mixture according to (a) comprises, preferably consists of, one or more of a phosphoric acid, a salt of a phosphoric acid, and an ester of a phosphoric acid, preferably one or more of orthophosphoric acid, phosphorous acid, metaphosphoric acid, polyphosphoric acid, diphosphoric acid, triphosphoric acid, tetraphosphor-

ic acid, trimetaphosphoric acid, tetrametaphosphoric acid, phosphorous pentoxide, ammonium dihydrogen phosphate, and diammonium hydrogen phosphate, more preferably diammonium hydrogen phosphate.

- 5 It is preferred that the source of P comprised in the reaction mixture according to (a) comprises, preferably consists of, a phosphoric acid, preferably orthophosphoric acid, wherein the phosphoric acid is preferably dissolved in an aqueous solution, preferably comprising an amount of phosphoric acid in the range of from 75 to 95 weight-%, more preferably in the range of from 80 to 90 weight-%, based on the total weight of the aqueous solution.

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It is preferred that the reaction mixture provided in (a) comprises the oxidizing agent, wherein the oxidizing agent preferably comprises one or more of H_2O_2 , S_8 , I_2 , O_3 , O_2 , F_2 , Cl_2 , $\text{S}_2\text{O}_8^{2-}$, HBiO_3 , MnO_2 , KMnO_4 , HNO_3 , NH_4NO_3 , NO_3^- , KClO_3 , CuO , MnO_4^- , OCl^- , NO_3^- , ClO_3^- , ClO_2^- , Au^{3+} , Pt^{2+} , Pb^{2+} , BrO_3^- , CrO_4^{2-} , $\text{Fe}(\text{CN})_6^{3-}$, Co^{3+} , Ni^{3+} , FeO_4^{2-} , AsO_4^{3-} , Cu^{2+} , Sn^{2+} , Pb^{4+} , As^{3+} , and Bi^{3+} , wherein the oxidizing agent more preferably comprises, more preferably consists of, one or more of HNO_3 , NH_4NO_3 , NO_3^- , wherein the oxidizing agent more preferably comprises, more preferably consists of, NO_3^- .

15

It is preferred that the reaction mixture provided in (a) further comprises one or more sources of an element E other than Nb, V, P, and O, preferably selected from groups 1 to 15 of the periodic system of elements and lanthanides, more preferably selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Sm, Ti, Zr, Hf, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, and Bi, more preferably selected from the group consisting of Ti, Zr, Hf, Ta, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Ge, Sn, Pb, Sb, and Bi, more preferably selected from the group consisting of Ta, Mo, W, Fe, Co, Ni, and Sb.

20

It is preferred that the reaction mixture provided in (a) as defined in embodiment 30 exhibits a molar ratio of the further element E to the sum of the further element E, Nb, V and P, $\text{E}:(\text{E}+\text{Nb}+\text{V}+\text{P})$, in the range of from equal to or smaller than 0.3:1, preferably in the range of from equal to or smaller than 0.2:1, more preferably in the range of from equal to or smaller than 0.1:1.

30

It is preferred that the process comprises drying according to (b) as defined in embodiment (30), wherein the temperature of the gas atmosphere in (b) is in the range of from 60 to 90 °C, preferably in the range of from 65 to 75 °C.

35

It is preferred that the process comprises drying according to (b) as defined in embodiment 30, wherein drying in (b) is performed for a duration in the range of from 1 to 24 h, preferably in the range of from 3 to 18 h, more preferably in the range of from 6 to 12 h.

40

It is preferred that the process comprises drying according to (b) as defined in embodiment 30, wherein the gas atmosphere in (b) comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

- 5 It is preferred that the gas atmosphere in (d) has a temperature in the range of from 350 to 750 °C, preferably in the range of from 400 to 700 °C.

It is preferred that the heat treatment in (d) is carried out for a duration in the range of from 6 h to 5 d, preferably in the range of from 12 h to 4 d.

10

It is preferred that the gas atmosphere in (d), preferably as defined in embodiment 41 or 42, comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

- 15 According to a first alternative, it is preferred that the reaction mixture provided in (a) further comprises a fuel component.

- In the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the reaction mixture according to (a) as defined herein exhibits a molar ratio of Nb to the sum of V, Nb, and P, Nb:(V+Nb+P), in the range of from 0.045:1 to 0.48:1, preferably in the range of from 0.083:1 to 0.46:1, more preferably in the range of from 0.5:1 to 0.45:1.

- 25 Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the reaction mixture according to (a) as defined herein exhibits a molar ratio of V to the sum of V, Nb, and P, V:(V+Nb+P), in the range of from 0.005:1 to 0.455:1, preferably in the range of from 0.024:1 to 0.33:1, more preferably in the range of from 0.04:1 to 0.21:1.

- 30 Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the reaction mixture provided in (a) as defined herein comprises the oxidizing agent, and that the reaction mixture provided in (a) exhibits a molar ratio of the oxidizing agent to the fuel component, oxidizing agent : fuel component, in the range of from 1:5 to 20:1, preferably in the range of from 1:2 to 10:1, more preferably in the range of from 1:1 to 6:1.

35

Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the fuel component has a decomposition temperature of equal to or higher than 200 °C, preferably in the range of from 200 to 500 °C, more preferably in the range of from 220 to 450 °C.

40

Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the fuel component comprises one or more of glycine, urea, carbonylhydrazide, oxalyl dihydrazide, malonic acid dihy-

drazide, urotropin, citric acid, maleic hydrazide, 1,2-diformylhydrazine, glucose, sucrose, stearic acid, ethylene glycol, ethanolamine, L-alpha-alanine, L-aspartic acid, L-valine, and L-leucine, wherein the fuel component preferably comprises, more preferably consists of, glycine.

- 5 Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the fuel component comprises, preferably consists of, glycine, and that the molar ratio of Nb to the fuel component, Nb:fuel component, in the reaction mixture provided in (a) as defined in embodiment (30) is in the range of from 0.05:1 to 1:1, preferably in the range of from 0.1:1 to 0.7:1, more preferably in
10 the range of from 0.13:1 to 0.67:1.

- Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the fuel component comprises, preferably consists of, glycine, and that the molar ratio of V to the fuel component, V:fuel component, in the reaction mixture provided in (a) as defined in embodiment (30) is in the
15 range of from 0.1:1 to 0.6:1, preferably in the range of from 0.25:1 to 0.40:1, more preferably in the range of from 0.29:1 to 0.33:1.

- Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the fuel component comprises, preferably consists of, glycine, and that the molar ratio of P to the fuel component, P:fuel component, in the reaction mixture provided in (a) as defined in embodiment (30) is in the
20 range of from 0.1:1 to 1.5:1, preferably in the range of from 0.35:1 to 1.1:1, more preferably in the range of from 0.45:1 to 0.96:1.

- 25 Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the thermal treatment in (c) as defined herein comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) in a gas atmosphere to the ignition temperature of the fuel component.
30

- Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the thermal treatment in (c) as defined herein comprises heating the reaction mixture obtained in (a) or the dried
35 reaction mixture obtained in (b) in a gas atmosphere to a temperature of at least 350 °C, preferably to a temperature of at least 375 °C, preferably to a temperature in the range of from 350 to 450 °C, more preferably in the range of from 390 to 410 °C.

- 40 Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that the thermal treatment in (c) as defined herein comprises a solution combustion synthesis.

Further in the case where the reaction mixture provided in (a) further comprises a fuel component according to the first alternative as described herein, it is preferred that tempering in (d) comprises, preferably consists of,

- 5 (d.1) subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature in the range of from 300 to 500 °C, preferably in the range of from 350 to 450 °C;
- (d.2) optionally subjecting the precursor of the mixed oxide obtained in (d.1) to a heat treatment in a gas atmosphere having a temperature in the range of from 400 to 600 °C, preferably in the range of from 450 to 550 °C;
- 10 (d.3) optionally subjecting the precursor of the mixed oxide obtained in (d.1) or (d.2) to a heat treatment in a gas atmosphere having a temperature in the range of from 500 to 700 °C, preferably in the range of from 550 to 650 °C;
- (d.4) optionally subjecting the precursor of the mixed oxide obtained in (d.1), (d.2) or (d.3) to a heat treatment in a gas atmosphere having a temperature in the range of from 600 to 800 °C, preferably in the range of from 650 to 750 °C.
- 15

In the case where tempering in (d) comprises, preferably consists of, (d.1), optionally (d.2), optionally (d.3), and optionally (d.4) according to the first alternative as described herein, it is preferred that the heat treatment in any one of (d.1), (d.2), (d.3), and (d.4) as defined herein, independently from one another, is carried out for a duration in the range of from 10 h to 40 d, preferably in the range of from 20 h to 28 d, more preferably in the range of from 23 h to 25 d.

20

Further in the case where tempering in (d) comprises, preferably consists of, (d.1), optionally (d.2), optionally (d.3), and optionally (d.4) according to the first alternative as described herein, it is preferred that the gas atmosphere in any one of (d.1), (d.2), (d.3), and (d.4) as defined herein, independently from one another, comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

25

According to a second alternative, it is preferred that the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, in the range of from 0.01:1 to 0.50:1, preferably in the range of from 0.05:1 to 0.20:1, more preferably in the range of from 0.10:1 to 0.12:1.

30

In the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the reaction mixture provided in (a) exhibits a molar ratio of V to water, V:water, in the range of from 0.001:1 to 2.0:1, preferably in the range of from 0.005:1 to 1.0:1, more preferably in the range of from 0.01:1 to 0.70:1.

35

Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the reaction mixture provided in (a) exhibits a molar ratio of P to water, P:water, in the range of from 0.05:1 to 0.50:1, preferably in the range of from 0.10:1 to 0.20:1, more preferably in the range of from 0.12:1 to 0.16:1.

40

Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the reaction mixture according to (a) exhibits a molar ratio of Nb:(Nb+V+P) in the range of from 0.167:1 to 0.455:1, preferably in the range of from 0.25:1 to 0.44:1, more preferably in the range of from 0.3:1 to 0.4375:1.

Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the reaction mixture according to (a) exhibits a molar ratio of V:(Nb+V+P) in the range of from 0.005:1 to 0.357:1, preferably in the range of from 0.024:1 to 0.25:1, more preferably in the range of from 0.045:1 to 0.167:1.

Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the thermal treatment in (c) comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) to a temperature of at least 150 °C, preferably to a temperature of at least 175 °C, preferably to a temperature in the range of from 175 to 225 °C, more preferably in the range of from 190 to 210 °C.

Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the thermal treatment in (c) comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) with a heating rate in the range of from 50 to 150 K/h, preferably in the range of from 75 to 125 K/h, more preferably in the range of from 90 to 110 K/h.

Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the thermal treatment in (c) comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) for a duration in the range of from 20 to 75 h, preferably in the range of from 40 to 55 h, more preferably in the range of from 47 to 49 h.

Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the thermal treatment in (c) is performed under autogenous pressure, preferably under solvothermal conditions, more preferably under hydrothermal conditions, wherein the thermal treatment in (c) is preferably performed in a pressure tight vessel, preferably in an autoclave.

Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that tempering in (d) as defined herein comprises, preferably consists of,

(d.1') subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature in the range of from 400 to 600 °C, preferably in the range of from 450 to 550 °C;

5 (d.2') optionally subjecting the precursor of the mixed oxide obtained in (d.1') to a heat treatment in a gas atmosphere having a temperature in the range of from 500 to 700 °C, preferably in the range of from 550 to 650 °C.

10 In the case where tempering in (d) as defined herein comprises, preferably consists of, (d.1'), and optionally (d.2'), according to the second alternative as described herein, it is preferred that the heat treatment in (d.1') or (d.2') independently from one another, is carried out for a duration in the range of from 10 h to 40 d, preferably in the range of from 20 h to 28 d, more preferably in the range of from 23 h to 25 d.

15 Further in the case where tempering in (d) as defined herein comprises, preferably consists of, (d.1'), and optionally (d.2'), according to the second alternative as described herein, it is preferred that the gas atmosphere in (d.1') or (d.2') independently from one another, comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

20 Further in the case where the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, according to the second alternative as described herein, it is preferred that the process further comprises (f) cooling the mixed oxide obtained from (d) as defined herein, (d.1') as defined herein, or (d.2') as defined herein in a gas atmosphere having a temperature in the range of from 10 to 40 °C, preferably in the range of from 20 to 30 °C.

25 In the case where the process further comprises (f) according to the second alternative as described herein, it is preferred that the gas atmosphere in (f) comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

30 Further in the case where the process further comprises (f) according to the second alternative as described herein, it is preferred that the cooling in (f) is carried out for a duration in the range of from 2 to 24 h, preferably in the range of from 6 to 12 h.

According to a third alternative, it is preferred that the process comprises after (a) and prior to (c) as defined herein,

35 (a') heating the reaction mixture obtained in (a) in a gas atmosphere having a temperature in the range of from 60 to 100 °C, preferably in the range of from 75 to 85 °C;

(a'') admixing a source of a support material to the reaction mixture obtained from (a'), wherein the process preferably does not comprise (b).

40 In the case where the process comprises after (a) and prior to (c) as defined herein (a') and (a''), it is preferred that the gas atmosphere in (a'), comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

Further in the case where the process comprises after (a) and prior to (c) as defined herein (a') and (a'') according to the third alternative, it is preferred that the reaction mixture obtained in (a'') exhibits a molar ratio of the source of a support material to Nb, support material:Nb, in the range of from 1:1 to 100:1, preferably in the range of from 5:1 to 45:1, more preferably in the range of from 7:1 to 42:1.

Further in the case where the process comprises after (a) and prior to (c) as defined herein (a') and (a'') according to the third alternative, it is preferred that the reaction mixture obtained in (a'') exhibits a molar ratio of the source of a support material to V, support material:V, in the range of from 1:1 to 50:1, preferably in the range of from 2:1 to 25:1, more preferably in the range of from 4:1 to 18:1.

Further in the case where the process comprises after (a) and prior to (c) as defined herein (a') and (a'') according to the third alternative, it is preferred that the reaction mixture obtained in (a'') exhibits a molar ratio of the source of a support material to P, support material:P, in the range of from 0.1:1 to 25:1, preferably in the range of from 1:1 to 10:1, more preferably in the range of from 2:1 to 6:1.

Further in the case where the process comprises after (a) and prior to (c) as defined herein (a') and (a'') according to the third alternative, it is preferred that the support material is selected from the group consisting of silica, alumina, silica-alumina, titania, silica-titania, alumina-titania, silica-alumina-titania, and a mixture of two or more thereof, wherein the support material preferably comprises, more preferably consists of, silica.

Further in the case where the process comprises after (a) and prior to (c) as defined herein (a') and (a'') according to the third alternative, it is preferred that the thermal treatment in (c) comprises heating the reaction mixture obtained in (a'') or the dried reaction mixture obtained in (b), preferably the reaction mixture obtained in (a''), to a temperature in the range of from 60 to 100 °C, preferably in the range of from 70 to 90 °C, more preferably in the range of from 75 to 85 °C.

Further in the case where the process comprises after (a) and prior to (c) as defined herein (a') and (a'') according to the third alternative, it is preferred that the thermal treatment in (c) comprises heating the reaction mixture obtained in (a'') or the dried reaction mixture obtained in (b), preferably the reaction mixture obtained in (a''), for a duration in the range of from 5 to 30 h, preferably in the range of from 12 to 20 h, more preferably in the range of from 15 to 17 h.

Further in the case where the process comprises after (a) and prior to (c) as defined herein (a') and (a'') according to the third alternative, it is preferred that tempering in (d) comprises, preferably consists of,

(d.1) subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature in the range of from 300 to 500 °C, preferably in the range of from 350 to 450 °C;

(d.2) optionally subjecting the precursor of the mixed oxide obtained in (d.1) to a heat treatment in a gas atmosphere having a temperature in the range of from 400 to 600 °C, preferably in the range of from 450 to 550 °C;

(d.3) optionally subjecting the precursor of the mixed oxide obtained in (d.1) or (d.2) to a heat treatment in a gas atmosphere having a temperature in the range of from 500 to 700 °C, preferably in the range of from 550 to 650 °C;

(d.4) optionally subjecting the precursor of the mixed oxide obtained in (d.1), (d.2) or (d.3) to a heat treatment in a gas atmosphere having a temperature in the range of from 600 to 800 °C, preferably in the range of from 650 to 750 °C.

In the case where the tempering in (d) comprises, preferably consists of, (d.1), optionally (d.2), optionally (d.3), and optionally (d.4) according to the third alternative, it is preferred that the heat treatment in any one of (d.1), (d.2), (d.3), and (d.4) as defined herein, independently from one another, is carried out for a duration in the range of from 10 h to 40 d, preferably in the range of from 20 h to 28 d, more preferably in the range of from 23 h to 25 d.

Further in the case where the tempering in (d) comprises, preferably consists of, (d.1), optionally (d.2), optionally (d.3), and optionally (d.4) according to the third alternative, it is preferred that the gas atmosphere in any one of (d.1), (d.2), (d.3), and (d.4) as defined herein, independently from one another, comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

It is preferred that the process further comprises

(e) subjecting the mixed oxide obtained in (d) to a heat treatment in a gas atmosphere having a temperature in the range of from 650 to 750 °C, preferably in the range of from 690 to 710 °C.

In the case where the process further comprises (e), it is preferred that the heat treatment in (e) is carried out for a duration in the range of from 0.5 to 7 d, preferably in the range of from 1 to 5 d, more preferably in the range of from 2 to 4 d.

Yet further, the present invention relates to a mixed oxide, preferably a mixed oxide according to any one of the embodiments disclosed herein, obtainable or obtained by a process according to any one of the embodiments disclosed herein.

Yet further, the present invention relates to a mixed oxide supported on a support material, preferably a mixed oxide according to any one of the embodiments disclosed herein supported on a support material, obtainable or obtained by a process according to any one of the embodiments disclosed herein.

Yet further, the present invention relates to a molding, comprising a mixed oxide according to any one of the embodiments disclosed herein and an oxidic binder.

In the case where the present invention relates to a molding, comprising a mixed oxide according to any one of the embodiments disclosed herein and an oxidic binder, it is preferred that the molding comprises the oxidic binder, calculated as the respective oxide, in an amount in the range of from 2 to 90 weight-%, more preferably in the range of from 5 to 70 weight-%, more preferably in the range of from 10 to 50 weight-%, more preferably in the range of from 15 to 30 weight-%, based on the total weight of the molding.

Further in the case where the present invention relates to a molding, comprising a mixed oxide according to any one of the embodiments disclosed herein and an oxidic binder, it is preferred that the oxidic binder preferably comprises one or more of zirconia, alumina, titania, silica and a mixed oxide comprising two or more of Zr, Al, Ti and Si, wherein the oxidic binder more preferably comprises one or more of alumina and silica, more preferably silica.

Further in the case where the present invention relates to a molding, comprising a mixed oxide according to any one of the embodiments disclosed herein and an oxidic binder, it is preferred that the molding is in the form of a tablet or an extrudate.

Yet further, the present invention relates to a use of a mixed oxide according to any one of the embodiments disclosed herein, or of a molding according to any one of the embodiments disclosed herein, as a catalyst or a catalyst component, preferably in a reaction for converting one or more hydrocarbons, preferably in an oxidation reaction, of one or more hydrocarbons, more preferably in a selective partial oxidation of one or more hydrocarbons, preferably substituted hydrocarbons, wherein the hydrocarbons preferably comprise, more preferably consist of, an alkane, an alkene, an aldehyde, a ketone, or an aromatic, wherein the hydrocarbons more preferably are selected from the group consisting of propanol, isopropanol, propionaldehyde, butanol, butyraldehyde, benzene, toluene, xylene, acrolein, methacrolein, ethane, ethylene, propane, propene, n-butane, but-1-ene, but-2-ene, isobutylene, 1,3-butadiene, isobutane, n-pentane, 1-pentene, 2-methyl-but-1-ene, 2-methyl-but-2-ene, 3-methyl-but-1-ene, and a mixture of two or more thereof, more preferably from the group consisting of ethane, ethylene, propane, propene, n-butane, but-1-ene, but-2-ene, isobutylene, 1,3-butadiene, isobutane, n-pentane, 1-pentene, 2-methyl-but-1-ene, 2-methyl-but-2-ene, 3-methyl-but-1-ene, and a mixture of two or more thereof, more preferably from the group consisting of propane, propene, n-butane, but-1-ene, but-2-ene, isobutylene, 1,3-butadiene, isobutane, and a mixture of two or more thereof, more preferably from the group consisting of propane, propene, n-butane, but-1-ene, but-2-ene, 1,3-butadiene, , and a mixture of two or more thereof, more preferably selected from the group consisting of propane, propene, n-butane, and a mixture of two or more thereof.

Yet further, the present invention relates to a process for the oxidation, preferably for the partial oxidation, more preferably for the selective partial oxidation, of one or more hydrocarbons, the process comprising

(A) providing a reactor comprising a reaction zone, wherein the reaction zone comprises a catalyst, said catalyst comprising a mixed oxide according to any one of the embodiments disclosed herein or a molding according to any one of the embodiments disclosed herein;

- (B) introducing a reaction gas stream in the reaction zone according to (A), wherein the reaction gas stream comprises the one or more hydrocarbons, oxygen (O₂), water (H₂O) and preferably one or more inert gases;
- (C) subjecting the reaction gas stream to oxidation conditions in the reaction zone according to (A);
- (D) separating a product gas stream from the reaction zone, wherein the product gas stream comprises at least one oxidation product of the one or more hydrocarbons.

It is preferred that the reaction zone comprises the mixed oxide or the molding in a fixed-bed.

It is preferred that the reactor comprises two or more reaction zones.

In the case where the reactor comprises two or more reaction zones, it is preferred that the two or more reaction zones are arranged in parallel to each other.

Further in the case where the reactor comprises two or more reaction zones, it is preferred that the two or more reaction zones are serially arranged.

It is preferred that the mixed oxide is comprised in a molding, preferably in the molding according to (A).

It is preferred that the mixed oxide or the molding is heated in (A) to a temperature in the range of from 150 to 350 °C, preferably in the range of from 170 to 330 °C, more preferably in the range of from 180 to 320 °C, more preferably in the range of from 190 to 310 °C.

It is preferred that the mixed oxide or the molding is heated in (B) to a temperature in the range of from 350 to 500 °C, preferably in the range of from 370 to 480 °C, more preferably in the range of from 380 to 470 °C, more preferably in the range of from 390 to 460 °C.

It is preferred that after (A) and prior to (B) the mixed oxide or the molding is heated to a temperature in the range of from 150 to 350 °C, preferably in the range of from 170 to 330 °C, more preferably in the range of from 180 to 320 °C, more preferably in the range of from 190 to 310 °C, and wherein in (B) the mixed oxide or the molding is heated to a temperature in the range of from 350 to 500 °C, preferably in the range of from 370 to 480 °C, more preferably in the range of from 380 to 470 °C, more preferably in the range of from 390 to 460 °C.

It is preferred that the hydrocarbons are selected from the group consisting of propanol, isopropanol, propanal, butanol, butyraldehyde, benzene, toluene, xylene, acrolein, methacrolein, ethane, ethylene, propane, propylene, n-butane, 1-butene, 2-butene, 1,3-butadiene, isobutene, isobutene, n-pentane, 1-pentene, 2-methyl-1-butene, isopentene, 3-methyl-1-butene, and a mixture of two or more thereof, preferably selected from the group consisting of ethane, ethylene, propane, propylene, n-butane, 1-butene, 2-butene, 1,3-butadiene, isobutane, isobutene, n-pentane, 1-pentene, 2-methyl-1-butene, isopentene, 3-methyl-1-butene, and a mixture of two or

more thereof, more preferably selected from the group consisting of propane, propylene, n-butane, 1-butene, 2-butene, 1,3-butadiene, isobutane, isobutene, and a mixture of two or more thereof, more preferably selected from the group consisting of propane, propylene, n-butane, 1-butene, 2-butene, 1,3-butadiene, and a mixture of two or more thereof, more preferably selected
5 from the group consisting of propane, propylene, n-butane, and a mixture of two or more thereof.

It is preferred that the reaction gas stream in (B) exhibits a volume ratio of the one or more hydrocarbons to oxygen (O_2) in the range of from 1:1 to 1:50, preferably in the range of from 1:2 to
10 1:35, more preferably in the range of from 1:3 to 1:31, more preferably in the range of from 1:4 to 1:20, more preferably in the range of from 1:7 to 1:18, more preferably in the range of from 1:9 to 1:16.

It is preferred that the reaction gas stream in (B) exhibits a volume ratio of the one or more hydrocarbons to water (H_2O) in the range of from 10:1 to 1:25, preferably in the range of from 5:1
15 to 1:20, more preferably in the range of from 2:1 to 1:10, more preferably in the range of from 1:1 to 1:5, more preferably in the range of from 1:2 to 1:4.

It is preferred that from 95 to 100 volume-%, preferably from 97 to 100 volume-%, more preferably from 98 to 100 volume-%, more preferably from 99 to 100 volume-%, of the reaction gas
20 stream introduced in (B) in the reaction zone consists of one or more hydrocarbons, oxygen (O_2), water (H_2O) and one or more inert gases.

It is preferred that the reaction gas stream in (B) comprises from 0.1 to 5.0 volume-% of hydrocarbons, preferably from 0.3 to 3.5 volume-%, more preferably from 0.5 to 2.5 volume-%, more
25 preferably from 0.75 to 2.25 volume-%, more preferably from 0.9 to 2.1 volume-%.

It is preferred that the reaction gas stream in (B) comprises from 5 to 25 volume-% of oxygen (O_2), preferably from 10 to 25 volume-%, more preferably from 12 to 23 volume-%, more preferably
30 ably from 14 to 21 volume-%.

It is preferred that the reaction gas stream in (B) comprises from 0.1 to 25 volume-% of water (H_2O), preferably from 0.5 to 20 volume-%, more preferably from 0.75 to 10 volume-%, more
35 preferably from 1 to 5 volume-%, more preferably from 2.5 to 3.5 volume-%.

It is preferred that the oxidation conditions in the reaction zone comprise a pressure in the range of from 0.5 to 5 bar(abs), preferably in the range of from 0.6 to 4 bar(abs), more preferably in
the range of from 0.7 to 3.5 bar(abs), more preferably in the range of from 0.9 to 3.1 bar(abs).

It is preferred that the oxidation conditions in the reaction zone comprise gas hourly space velocity of the reaction gas stream based on the volume of the mixed oxide or the molding provided
40 in (A) in the range of from 300 to 100 000 h^{-1} , preferably in the range of from 1 000 to 10 000 h^{-1} , more preferably in the range of from 1 500 to 6 000 h^{-1} .

It is preferred that the inert gases comprise nitrogen (N₂), argon, or a mixture thereof, preferably nitrogen (N₂) and argon, wherein the inert gases more preferably consist of nitrogen (N₂) and argon.

5

It is preferred that from 95 to 100 volume-%, preferably from 96 to 100 volume-%, more preferably from 98 to 100 volume-%, more preferably from 99 to 100 volume-%, of the inert gases consists of nitrogen (N₂) and argon.

10 It is preferred that from 1 to 5 volume-%, preferably from 2 to 4 volume-%, of the inert gases comprise, preferably consist of, argon.

It is preferred that the oxidation conditions are isothermal.

15 It is preferred that the reaction gas stream comprises propane or propylene and the product gas stream comprises acrolein, acrylic acid or a mixture thereof.

It is preferred that the reaction gas stream comprises n-butane and the product gas stream comprises maleic anhydride.

20

According to the present invention, a crystalline phase, e. g. a VOPO₄ crystalline phase, can be understood as showing characteristic bragg peaks according to Bragg's law ($n\lambda = 2d \sin(\theta)$) in a recorded X-ray diffraction pattern. For characterizing the mixed oxides of the present invention, they were analyzed also by X-ray diffraction. An amorphous phase or region of a sample produces a broad peak in a recorded X-ray diffraction pattern, whereas crystalline regions produce sharp peaks. Such a broad peak can also be seen as diffuse scattering (seen as modulation of the background).

25

X-ray diffraction technique is also useful for determining the percent crystallinity. The degree of crystallinity can be determined by determining the intensities of the crystalline and amorphous contents in a sample. In this regard, different methods are known, e. g. relative intensity ratio method (RIR) or external standard addition method. In particular with respect to the determination of low amounts of amorphous VOPO₄, such low amounts can be detected by electron microscopy with coupled elemental analysis (HRTEM+EDX).

35

The unit bar(abs) refers to an absolute pressure of 10⁵ Pa, and the unit Angstrom refers to a length of 10⁻¹⁰ m.

40

The present invention is further illustrated by the following set of embodiments, and combinations of embodiments resulting from the dependencies and back-references as indicated. In particular, it is noted that in each instance where a range of embodiments is mentioned, for example in the context of a term such as "any one of embodiments (1) to (4)", every embodiment in this range is meant to be explicitly disclosed for the skilled person, i.e. the wording of this

term is to be understood by the skilled person as being synonymous to "any one of embodiments (1), (2), (3), and (4)". Further, it is explicitly noted that the following set of embodiments is not the set of claims determining the extent of protection, but represents a suitably structured part of the description directed to general and preferred aspects of the present invention.

5

According to an embodiment (1), the present invention relates to a mixed oxide comprising Nb, V, P, and O, exhibiting a molar ratio of Nb to the sum of Nb and V, Nb:(Nb+V), of equal to or greater than 0.091:1, comprising a crystalline NbOPO₄ phase, and comprising a crystalline alpha(II) VOPO₄ phase in an amount in the range of from equal to or greater than 50 weight-%, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, preferably determined as described in Reference Example 1, wherein the crystalline NbOPO₄ phase and/or the crystalline alpha(II) VOPO₄ phase and the respective amounts thereof are more preferably determined as described in Reference Example 1.

10

15 A preferred embodiment (2) concretizing embodiment (1) relates to said mixed oxide, wherein the crystalline alpha(II) VOPO₄ phase exhibits an X-ray diffraction pattern comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
110	19.33 – 21.16
111	28.77 – 29.68
200	27.60 – 29.99

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1,

20 preferably comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
001	19.83 – 21.84
110	19.43 – 21.06
101	24.79 – 25.98
111	28.87 – 29.58
200	27.70 – 29.89

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1,

more preferably comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
001	19.93 – 21.74
110	19.53 – 20.96
101	24.89 – 25.88
111	28.97 – 29.48
200	27.80 – 29.79

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1.

5 A further preferred embodiment (3) concretizing embodiment (1) or (2) relates to said mixed oxide, wherein the mixed oxide further comprises amorphous VOPO_4 in a total amount in the range of from 0 to 1 weight-%, preferably in the range of from 0 to 0.5 weight-%, more preferably in the range of from 0 to 0.1 weight-%, based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 , preferably determined via electron microscopy with coupled elemental analysis, more preferably by high-resolution transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (HRTEM coupled with EDX).
10

A further preferred embodiment (4) concretizing any one of embodiments (1) to (3) relates to said mixed oxide, wherein the mixed oxide further comprises one or more crystalline VOPO_4 phases other than the crystalline $\alpha(\text{II})$ VOPO_4 phase in a total amount in the range of from 0 to 1 weight-%, preferably in the range of from 0 to 0.5 weight-%, more preferably in the range of from 0 to 0.1 weight-%, based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 .
15

A further preferred embodiment (5) concretizing any one of embodiments (1) to (4) relates to said mixed oxide, wherein the mixed oxide exhibits a molar ratio of Nb to the sum of V, Nb, and P, $\text{Nb}:(\text{V}+\text{Nb}+\text{P})$, of equal to or greater than 0.1:1, preferably of equal to or greater than 0.14:1, more preferably in the range of from 0.167:1 to 0.495:1, more preferably in the range of from 0.1875:1 to 0.49:1, more preferably in the range of from 0.24:1 to 0.48:1, more preferably in the range of from 0.3:1 to 0.469:1, more preferably in the range of from 0.33:1 to 0.45:1, more preferably in the range of from 0.344:1 to 0.45:1.
20
25

A further preferred embodiment (6) concretizing any one of embodiments (1) to (5) relates to said mixed oxide, wherein the mixed oxide comprises the crystalline $\alpha(\text{II})$ VOPO_4 phase in an amount in the range of from 50 to 88.8 weight-%, preferably in the range of from 60 to 84 weight-%, more preferably in the range of from 70 to 80 weight-%, based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 , preferably determined as described in Reference Example 1.
30

A further preferred embodiment (7) concretizing any one of embodiments (1) to (6) relates to said mixed oxide, wherein the mixed oxide exhibits a molar ratio of V to the sum of V, Nb, and P, $\text{V}:(\text{V}+\text{Nb}+\text{P})$, in the range of from 0.005:1 to 0.495:1, preferably in the range of from 0.01:1 to 0.35:1, more preferably in the range of from 0.015:1 to 0.25:1, more preferably in the range of from 0.025:1 to 0.2:1, more preferably in the range of from 0.045:1 to 0.155:1.
35

A further preferred embodiment (8) concretizing any one of embodiments (1) to (7) relates to said mixed oxide, wherein the mixed oxide exhibits a molar ratio of P to the sum of V, Nb, and P, $\text{P}:(\text{V}+\text{Nb}+\text{P})$, in the range of from 0.40:1 to 0.60:1, more preferably in the range of from 0.45:1 to 0.55:1, more preferably in the range of from 0.49:1 to 0.51:1.
40

A further preferred embodiment (9) concretizing any one of embodiments (1) to (8) relates to said mixed oxide, wherein from 90 to 100 weight-%, preferably from 95 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.9 to 100 weight-%, of the mixed oxide consist of V, Nb, P, O, and H.

A further preferred embodiment (10) concretizing any one of embodiments (1) to (9) relates to said mixed oxide, wherein the mixed oxide comprises from 0 to 10 weight-%, preferably from 0 to 5 weight-%, more preferably from 0 to 1 weight-%, more preferably from 0 to 0.1 weight-%, more preferably from 0 to 0.01 weight-%, more preferably from 0 to 0.001 weight-%, of a crystalline $(VO)_2P_2O_7$ (vanadyl pyrophosphate) phase, based on the sum of the weight of Nb calculated as $NbOPO_4$ and of V calculated as $VOPO_4$, preferably determined as described in Reference Example 1.

A further preferred embodiment (11) concretizing embodiment (10) relates to said mixed oxide, wherein the crystalline $(VO)_2P_2O_7$ (vanadyl pyrophosphate) phase exhibits an X-ray diffraction pattern comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
012	13.91 – 14.31
111	15.44 – 15.84
020	18.29 – 18.69
200	22.77 – 23.17
024	28.23 – 28.63
032	29.74 – 30.14
016	33.51 – 33.91
224	36.66 – 37.06
036	43.03 – 43.43
400	46.73 – 47.13

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1,

preferably comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
012	14.01 – 14.21
111	15.54 – 15.74
020	18.39 – 18.59
200	22.87 – 23.07
024	28.33 – 28.53
032	29.84 – 30.04
016	33.61 – 33.81
224	36.76 – 36.96
036	43.13 – 43.33

400	46.83 – 47.03
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wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1.

5 A further preferred embodiment (12) concretizing any one of embodiments (1) to (11) relates to said mixed oxide, wherein the mixed oxide is essentially free of a crystalline $(VO)_2P_2O_7$ (vanadyl pyrophosphate) phase.

10 A further preferred embodiment (13) concretizing any one of embodiments (1) to (12) relates to said mixed oxide, wherein the mixed oxide comprises, preferably consisting of, a solid solution.

15 A further preferred embodiment (14) concretizing embodiment (13) relates to said mixed oxide, wherein the solvent is the crystalline $\alpha(II)$ $VOPO_4$ phase, calculated as $VOPO_4$, if the amount of said crystalline phase in the mixed oxide is higher than the amount of the crystalline α $NbOPO_4$ phase, calculated as $NbOPO_4$, in the mixed oxide, based on the sum of the weight of Nb calculated as $NbOPO_4$ and of V calculated as $VOPO_4$, wherein the amount of a crystalline phase is preferably determined as described in Reference Example 1.

20 A further preferred embodiment (15) concretizing embodiment (13) relates to said mixed oxide, wherein the solute is the crystalline $\alpha(II)$ $VOPO_4$ phase if the amount of said crystalline phase in the mixed oxide is smaller than the amount of the crystalline α $NbOPO_4$ phase in the mixed oxide, based on the sum of the weight of Nb calculated as $NbOPO_4$ and of V calculated as $VOPO_4$, wherein the amount of a crystalline phase is preferably determined as described in Reference Example 1.

25 A further preferred embodiment (16) concretizing any one of embodiments (1) to (15) relates to said mixed oxide, wherein the mixed oxide comprises the crystalline $NbOPO_4$ phase in an amount of less than 50 weight-%, preferably in the range of from 16 to 40 weight-%, more preferably in the range of from 20 to 30 weight-%, based on the sum of the weight of Nb calculated as $NbOPO_4$ and of V calculated as $VOPO_4$, preferably determined as described in Reference Example 1.

35 A further preferred embodiment (17) concretizing any one of embodiments (1) to (16) relates to said mixed oxide, wherein the crystalline $NbOPO_4$ phase comprises from 75 to 100 weight-%, preferably from 85 to 100 weight-%, more preferably from 90 to 100 weight-%, more preferably from 95 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.9 to 100 weight-%, of a crystalline α $NbOPO_4$ phase, based on the sum of the weight of Nb calculated as $NbOPO_4$ and of V calculated as $VOPO_4$, preferably determined as described in Reference Example 1.

40 A further preferred embodiment (18) concretizing any one of embodiments (1) to (17) relates to said mixed oxide, wherein the crystalline $NbOPO_4$ phase comprises from 0 to 25 weight-%, preferably from 0.1 to 15 weight-%, more preferably from 1 to 10 weight-%, more preferably from

4 to 5 weight-%, of a crystalline beta NbOPO₄ phase, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, preferably determined as described in Reference Example 1.

- 5 A further preferred embodiment (19) concretizing any one of embodiments (1) to (18) relates to said mixed oxide, wherein the crystalline beta NbOPO₄ phase exhibits an X-ray diffraction pattern comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
110	15.30 – 15.70
200	15.50 – 15.90
210	20.46 – 20.86
011	21.29 – 21.69
111	22.71 – 23.11
211	26.52 – 26.92
310	27.04 – 27.44
121	32.64 – 33.04
002	33.70 – 34.10
401	35.86 – 36.26

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1,

- 10 preferably comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
110	15.40 – 15.60
200	15.60 – 15.80
210	20.56 – 20.76
011	21.39 – 21.59
111	22.81 – 23.01
211	26.62 – 26.82
310	27.14 – 27.34
121	32.74 – 32.94
002	33.80 – 34.00
401	35.96 – 36.16

wherein the X-ray diffraction pattern is preferably determined according to Reference Example 1.

- 15 A further preferred embodiment (20) concretizing any one of embodiments (1) to (19) relates to said mixed oxide, wherein the mixed oxide comprises a crystalline phase of a metaphosphate anion, a polyphosphate anion, or a mixture of two or more thereof, preferably of a diphosphate anion, a triphosphate anion, a tetraphosphate anion, a trimetaphosphate anion, a tetrametaphosphate anion, or a mixture of two or more thereof, and one or more of NbO³⁺ and VO³⁺.

- A further preferred embodiment (21) concretizing embodiment (20) relates to said mixed oxide, wherein the mixed oxide comprises the crystalline phase of the metaphosphate anion, the polyphosphate, or the mixture of two or more thereof, preferably of the diphosphate anion, the triphosphate anion, the tetraphosphate anion, the trimetaphosphate anion, the tetrametaphosphate anion, or the mixture of two or more thereof, and of the one or more of NbO^{3+} and VO^{3+} , in an amount in the range of from 0 to 2 weight-%, preferably in the range of from 0.01 to 1 weight-%, more preferably in the range of from 0.1 to 0.5 weight-%, based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 .
- 10 A further preferred embodiment (22) concretizing any one of embodiments (1) to (21) relates to said mixed oxide, wherein the mixed oxide further comprises one or more of an element E other than Nb, V, P, and O, preferably selected from groups 1 to 15 of the periodic system of elements including lanthanides, more preferably selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Sm, Ti, Zr, Hf, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, and Bi, more preferably selected from the group consisting of Ti, Zr, Hf, Ta, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Ge, Sn, Pb, Sb, and Bi, more preferably selected from the group consisting of Ta, Mo, W, Fe, Co, Ni, and Sb.
- 15 20 A further preferred embodiment (23) concretizing embodiment (22) relates to said mixed oxide, wherein the mixed oxide comprises the one or more of an element E in an amount in the range of from 0.1 to 10 weight-%, preferably in the range of from 1 to 7.5 weight-%, more preferably in the range of from 2.5 to 5 weight-%, calculated as element and based on the sum of the weight of Nb calculated as NbOPO_4 and of V calculated as VOPO_4 .
- 25 A further preferred embodiment (24) concretizing any one of embodiments (1) to (23) relates to said mixed oxide, wherein the mixed oxide is a tempered mixed oxide, wherein the tempering was carried out by subjecting the mixed oxide to a heat treatment in a gas atmosphere, said gas atmosphere preferably comprising, more preferably consisting of, air, dry air, nitrogen, argon, or a mixture of two or more thereof, wherein the temperature of the gas atmosphere during the heat treatment is in the range of from 350 to 750 °C, preferably in the range of from 400 to 700 °C, and wherein the heat treatment was preferably carried out for a duration in the range of from 6 h to 5 d, preferably in the range of from 12 h to 4 d.
- 30 35 A further preferred embodiment (25) concretizing any one of embodiments (1) to (23) relates to said mixed oxide, wherein the mixed oxide was not subjected to a heat treatment as defined in embodiment (24).
- A further preferred embodiment (26) concretizing any one of embodiments (1) to (25) relates to said mixed oxide, wherein the mixed oxide has a BET specific surface area in the range of from 1 to 100 m^2/g , preferably in the range of from 3 to 75 m^2/g , more preferably in the range of from 10 to 50 m^2/g , preferably determined according to Reference Example 3.
- 40

A further preferred embodiment (27) concretizing any one of embodiments (1) to (26) relates to said mixed oxide, wherein the mixed oxide is supported on a support material.

5 A further preferred embodiment (28) concretizing embodiment (27) relates to said mixed oxide, wherein the support material is selected from the group consisting of silica, alumina, silica-alumina, titania, silica-titania, alumina-titania, silica-alumina-titania, and a mixture of two or more thereof, wherein the support material preferably comprises, more preferably consists of, silica.

10 A further preferred embodiment (29) concretizing embodiment (27) or (28) relates to said mixed oxide, wherein the support material has a BET specific surface area in the range of from 1 to 300 m²/g, preferably in the range of from 3 to 300 m²/g, more preferably in the range of from 10 to 200 m²/g preferably determined according to Reference Example 3.

15 An embodiment (30) of the present invention relates to a process for preparing a mixed oxide comprising Nb, V, P, and O, preferably for preparing a mixed oxide according to any one of embodiments (1) to (29), the process comprising

- (a) providing a reaction mixture comprising a source of Nb, a source of V, a source of P, water, and optionally an oxidizing agent;
- 20 (b) optionally drying the reaction mixture obtained in (a) in a gas atmosphere having a temperature in the range of from 50 to 100 °C, obtaining a dried reaction mixture;
- (c) subjecting the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) to a thermal treatment in a gas atmosphere, obtaining a precursor of the mixed oxide;
- 25 (d) subjecting the precursor of the mixed oxide obtained in (c) to tempering, said tempering comprising, preferably consisting of, subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature of at least 300 °C, obtaining the mixed oxide.

30 A preferred embodiment (31) concretizing embodiment (30) relates to said process, wherein the source of Nb comprises, preferably consists of, one or more of ammonium niobate(V) oxalate, niobium monoxide, niobium dioxide, niobium pentoxide, lithium niobate, potassium niobate, niobium(III) chloride, niobium(V) chloride, niobium carbide, niobium oxychloride, and niobium ethoxide, wherein the source of Nb preferably comprises, more preferably consists of, ammonium niobate(V) oxalate, preferably ammonium niobate(V) oxalate hydrate.

35 A further preferred embodiment (32) concretizing embodiment (30) or (31) relates to said process, wherein the source of V comprises, preferably consists of, one or more of an ammonium orthovanadate, an ammonium divanadate, an ammonium metavanadate, and an ammonium polyvanadate, wherein the source of V preferably comprises, more preferably consists of, an ammonium metavanadate.

40 A further preferred embodiment (33) concretizing any one of embodiments (30) to (32) relates to said process, wherein the source of P comprises, preferably consists of, one or more of a phosphoric acid, a salt of a phosphoric acid, and an ester of a phosphoric acid, preferably one or

more of orthophosphoric acid, phosphorous acid, metaphosphoric acid, polyphosphoric acid, diphosphoric acid, triphosphoric acid, tetraphosphoric acid, trimetaphosphoric acid, tetrametaphosphoric acid, phosphorous pentoxide, ammonium dihydrogen phosphate, and diammonium hydrogen phosphate, more preferably diammonium hydrogen phosphate.

5

A further preferred embodiment (34) concretizing any one of embodiments (30) to (33) relates to said process, wherein the source of P comprises, preferably consists of, a phosphoric acid, preferably orthophosphoric acid, wherein the phosphoric acid is preferably dissolved in an aqueous solution, preferably comprising an amount of phosphoric acid in the range of from 75 to 95 weight-%, more preferably in the range of from 80 to 90 weight-%, based on the total weight of the aqueous solution.

10

A further preferred embodiment (35) concretizing any one of embodiments (30) to (34) relates to said process, wherein the reaction mixture provided in (a) comprises the oxidizing agent, wherein the oxidizing agent preferably comprises one or more of H_2O_2 , S_8 , I_2 , O_3 , O_2 , F_2 , Cl_2 , $\text{S}_2\text{O}_8^{2-}$, HBiO_3 , MnO_2 , KMnO_4 , HNO_3 , NH_4NO_3 , NO_3^- , KClO_3 , CuO , MnO_4^- , OCl^- , NO_3^- , ClO_3^- , ClO_2^- , Au^{3+} , Pt^{2+} , Pb^{2+} , BrO_3^- , CrO_4^{2-} , $\text{Fe}(\text{CN})_6^{3-}$, Co^{3+} , Ni^{3+} , FeO_4^{2-} , AsO_4^{3-} , Cu^{2+} , Sn^{2+} , Pb^{4+} , As^{3+} , and Bi^{3+} , wherein the oxidizing agent more preferably comprises, more preferably consists of, one or more of HNO_3 , NH_4NO_3 , NO_3^- , wherein the oxidizing agent more preferably comprises, more preferably consists of, NO_3^- .

15

20

A further preferred embodiment (36) concretizing any one of embodiments (30) to (35) relates to said process, wherein the reaction mixture provided in (a) further comprises one or more sources of an element E other than Nb, V, P, and O, preferably selected from groups 1 to 15 of the periodic system of elements and lanthanides, more preferably selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Sm, Ti, Zr, Hf, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, and Bi, more preferably selected from the group consisting of Ti, Zr, Hf, Ta, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Ge, Sn, Pb, Sb, and Bi, more preferably selected from the group consisting of Ta, Mo, W, Fe, Co, Ni, and Sb.

25

30

A further preferred embodiment (37) concretizing embodiment (36) relates to said process, wherein the reaction mixture provided in (a) as defined in embodiment 30 exhibits a molar ratio of the further element E to the sum of the further element E, Nb, V and P, $\text{E}:(\text{E}+\text{Nb}+\text{V}+\text{P})$, in the range of from equal to or smaller than 0.3:1, preferably in the range of from equal to or smaller than 0.2:1, more preferably in the range of from equal to or smaller than 0.1:1.

35

A further preferred embodiment (38) concretizing any one of embodiments (30) to (37) relates to said process, wherein the process comprises drying according to (b) as defined in embodiment (30), wherein the temperature of the gas atmosphere in (b) is in the range of from 60 to 90 °C, preferably in the range of from 65 to 75 °C.

40

A further preferred embodiment (39) concretizing any one of embodiments (30) to (38) relates to said process, wherein the process comprises drying according to (b) as defined in embodiment 30, wherein drying in (b) is performed for a duration in the range of from 1 to 24 h, preferably in the range of from 3 to 18 h, more preferably in the range of from 6 to 12 h.

5

A further preferred embodiment (40) concretizing any one of embodiments (30) to (39) relates to said process, wherein the process comprises drying according to (b) as defined in embodiment 30, wherein the gas atmosphere in (b) comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

10

A further preferred embodiment (41) concretizing any one of embodiments (30) to (40) relates to said process, wherein the gas atmosphere in (d) has a temperature in the range of from 350 to 750 °C, preferably in the range of from 400 to 700 °C.

15 A further preferred embodiment (42) concretizing any one of embodiments (30) to (41) relates to said process, wherein the heat treatment in (d) is carried out for a duration in the range of from 6 h to 5 d, preferably in the range of from 12 h to 4 d.

20 A further preferred embodiment (43) concretizing any one of embodiments (30) to (42) relates to said process, wherein the gas atmosphere in (d), preferably as defined in embodiment 41 or 42, comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

A further preferred embodiment (44) concretizing any one of embodiments (30) to (43) relates to said process, wherein the reaction mixture provided in (a) further comprises a fuel component.

25

A further preferred embodiment (45) concretizing embodiment (44) relates to said process, wherein the reaction mixture according to (a) as defined in embodiment 30 exhibits a molar ratio of Nb to the sum of V, Nb, and P, $Nb:(V+Nb+P)$, in the range of from 0.045:1 to 0.48:1, preferably in the range of from 0.083:1 to 0.46:1, more preferably in the range of from 0.5:1 to 0.45:1.

30

A further preferred embodiment (46) concretizing embodiment (44) or (45) relates to said process, wherein the reaction mixture according to (a) as defined in embodiment 30 exhibits a molar ratio of V to the sum of V, Nb, and P, $V:(V+Nb+P)$, in the range of from 0.005:1 to 0.455:1, preferably in the range of from 0.024:1 to 0.33:1, more preferably in the range of from 0.04:1 to 0.21:1.

35

A further preferred embodiment (47) concretizing any one of embodiments (44) to (46) relates to said process, wherein the reaction mixture provided in (a) as defined in embodiment 30 comprises the oxidizing agent, and wherein the reaction mixture provided in (a) exhibits a molar ratio of the oxidizing agent to the fuel component, oxidizing agent : fuel component, in the range of from 1:5 to 20:1, preferably in the range of from 1:2 to 10:1, more preferably in the range of from 1:1 to 6:1.

40

A further preferred embodiment (48) concretizing any one of embodiments (44) to (47) relates to said process, wherein the fuel component has a decomposition temperature of equal to or higher than 200 °C, preferably in the range of from 200 to 500 °C, more preferably in the range of from 220 to 450 °C.

5

A further preferred embodiment (49) concretizing any one of embodiments (44) to (48) relates to said process, wherein the fuel component comprises one or more of glycine, urea, carbonyldi-
hydrazide, oxalyl dihydrazide, malonic acid dihydrazide, urotropin, citric acid, maleic hydrazide, 1,2-
diformylhydrazine, glucose, sucrose, stearic acid, ethylene glycol, ethanolamine, L-alpha-
alanine, L-aspartic acid, L-valine, and L-leucine, wherein the fuel component preferably com-
prises, more preferably consists of, glycine.

10

A further preferred embodiment (50) concretizing any one of embodiments (44) to (49) relates to said process, wherein the fuel component comprises, preferably consists of, glycine, and
wherein the molar ratio of Nb to the fuel component, Nb:fuel component, in the reaction mixture
provided in (a) as defined in embodiment (30) is in the range of from 0.05:1 to 1:1, preferably in
the range of from 0.1:1 to 0.7:1, more preferably in the range of from 0.13:1 to 0.67:1.

15

A further preferred embodiment (51) concretizing any one of embodiments (44) to (50) relates to said process, wherein the fuel component comprises, preferably consists of, glycine, and
wherein the molar ratio of V to the fuel component, V:fuel component, in the reaction mixture
provided in (a) as defined in embodiment (30) is in the range of from 0.1:1 to 0.6:1, preferably in
the range of from 0.25:1 to 0.40:1, more preferably in the range of from 0.29:1 to 0.33:1.

20

A further preferred embodiment (52) concretizing any one of embodiments (44) to (51) relates to said process, wherein the fuel component comprises, preferably consists of, glycine, and
wherein the molar ratio of P to the fuel component, P:fuel component, in the reaction mixture
provided in (a) as defined in embodiment (30) is in the range of from 0.1:1 to 1.5:1, preferably in
the range of from 0.35:1 to 1.1:1, more preferably in the range of from 0.45:1 to 0.96:1.

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A further preferred embodiment (53) concretizing any one of embodiments (44) to (52) relates to said process, wherein the thermal treatment in (c) as defined in embodiment (30) comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) in a gas atmosphere to the ignition temperature of the fuel component.

35

A further preferred embodiment (54) concretizing any one of embodiments (44) to (53) relates to said process, wherein the thermal treatment in (c) as defined in embodiment (30) comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) in a gas atmosphere to a temperature of at least 350 °C, preferably to a temperature of at least 375 °C,
preferably to a temperature in the range of from 350 to 450 °C, more preferably in the range of
from 390 to 410 °C.

40

A further preferred embodiment (55) concretizing any one of embodiments (44) to (54) relates to said process, wherein the thermal treatment in (c) as defined in embodiment 30 comprises a solution combustion synthesis.

5 A further preferred embodiment (56) concretizing any one of embodiments (44) to (55) relates to said process, wherein tempering in (d) comprises, preferably consists of,

(d.1) subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature in the range of from 300 to 500 °C, preferably in the range of from 350 to 450 °C;

10 (d.2) optionally subjecting the precursor of the mixed oxide obtained in (d.1) to a heat treatment in a gas atmosphere having a temperature in the range of from 400 to 600 °C, preferably in the range of from 450 to 550 °C;

(d.3) optionally subjecting the precursor of the mixed oxide obtained in (d.1) or (d.2) to a heat treatment in a gas atmosphere having a temperature in the range of from 500 to 700 °C, preferably in the range of from 550 to 650 °C;

15 (d.4) optionally subjecting the precursor of the mixed oxide obtained in (d.1), (d.2) or (d.3) to a heat treatment in a gas atmosphere having a temperature in the range of from 600 to 800 °C, preferably in the range of from 650 to 750 °C.

20 A further preferred embodiment (57) concretizing embodiment (56) relates to said process, wherein the heat treatment in any one of (d.1), (d.2), (d.3), and (d.4) as defined in embodiment (56), independently from one another, is carried out for a duration in the range of from 10 h to 40 d, preferably in the range of from 20 h to 28 d, more preferably in the range of from 23 h to 25 d.

25 A further preferred embodiment (58) concretizing embodiment (56) or (57) relates to said process, wherein the gas atmosphere in any one of (d.1), (d.2), (d.3), and (d.4) as defined in embodiment (56) or (57), independently from one another, comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

30 A further preferred embodiment (59) concretizing any one of embodiments (30) to (43) relates to said process, wherein the reaction mixture provided in (a) exhibits a molar ratio of Nb to water, Nb:water, in the range of from 0.01:1 to 0.50:1, preferably in the range of from 0.05:1 to 0.20:1, more preferably in the range of from 0.10:1 to 0.12:1.

35 A further preferred embodiment (60) concretizing embodiment (59) relates to said process, wherein the reaction mixture provided in (a) exhibits a molar ratio of V to water, V:water, in the range of from 0.001:1 to 2.0:1, preferably in the range of from 0.005:1 to 1.0:1, more preferably in the range of from 0.01:1 to 0.70:1.

40 A further preferred embodiment (61) concretizing embodiment (59) or (60) relates to said process, wherein the reaction mixture provided in (a) exhibits a molar ratio of P to water, P:water,

in the range of from 0.05:1 to 0.50:1, preferably in the range of from 0.10:1 to 0.20:1, more preferably in the range of from 0.12:1 to 0.16:1.

5 A further preferred embodiment (62) concretizing any one of embodiments (59) to (61) relates to said process, wherein the reaction mixture according to (a) exhibits a molar ratio of Nb:(Nb+V+P) in the range of from 0.167:1 to 0.455:1, preferably in the range of from 0.25:1 to 0.44:1, more preferably in the range of from 0.3:1 to 0.4375:1.

10 A further preferred embodiment (63) concretizing any one of embodiments (59) to (62) relates to said process, wherein the reaction mixture according to (a) exhibits a molar ratio of V:(Nb+V+P) in the range of from 0.005:1 to 0.357:1, preferably in the range of from 0.024:1 to 0.25:1, more preferably in the range of from 0.045:1 to 0.167:1.

15 A further preferred embodiment (64) concretizing any one of embodiments (59) to (63) relates to said process, wherein the thermal treatment in (c) comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) to a temperature of at least 150 °C, preferably to a temperature of at least 175 °C, preferably to a temperature in the range of from 175 to 225 °C, more preferably in the range of from 190 to 210 °C.

20 A further preferred embodiment (65) concretizing any one of embodiments (59) to (64) relates to said process, wherein the thermal treatment in (c) comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) with a heating rate in the range of from 50 to 150 K/h, preferably in the range of from 75 to 125 K/h, more preferably in the range of from 90 to 110 K/h.

25 A further preferred embodiment (66) concretizing any one of embodiments (59) to (65) relates to said process, wherein the thermal treatment in (c) comprises heating the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) for a duration in the range of from 20 to 75 h, preferably in the range of from 40 to 55 h, more preferably in the range of from 47 to 49 h.

30 A further preferred embodiment (67) concretizing any one of embodiments (59) to (66) relates to said process, wherein the thermal treatment in (c) is performed under autogenous pressure, preferably under solvothermal conditions, more preferably under hydrothermal conditions, wherein the thermal treatment in (c) is preferably performed in a pressure tight vessel, preferably in an autoclave.

A further preferred embodiment (68) concretizing any one of embodiments (59) to (67) relates to said process, wherein tempering in (d) as defined in embodiment (30) comprises, preferably consists of,
40 (d.1') subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature in the range of from 400 to 600 °C, preferably in the range of from 450 to 550 °C;

(d.2') optionally subjecting the precursor of the mixed oxide obtained in (d.1') to a heat treatment in a gas atmosphere having a temperature in the range of from 500 to 700 °C, preferably in the range of from 550 to 650 °C.

5 A further preferred embodiment (69) concretizing embodiment (68) relates to said process, wherein the heat treatment in (d.1') or (d.2') independently from one another, is carried out for a duration in the range of from 10 h to 40 d, preferably in the range of from 20 h to 28 d, more preferably in the range of from 23 h to 25 d.

10 A further preferred embodiment (70) concretizing embodiment (68) or (69) relates to said process, wherein the gas atmosphere in (d.1') or (d.2') independently from one another, comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

A further preferred embodiment (71) concretizing any one of embodiments (59) to (70) relates to
15 said process, wherein the process further comprises (f) cooling the mixed oxide obtained from (d) as defined in embodiment (30), (d.1') as defined in embodiment (68), or (d.2') as defined in embodiment (68) in a gas atmosphere having a temperature in the range of from 10 to 40 °C, preferably in the range of from 20 to 30 °C.

20 A further preferred embodiment (72) concretizing embodiment (71) relates to said process, wherein the gas atmosphere in (f) comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

A further preferred embodiment (73) concretizing embodiment (71) or (72) relates to said pro-
25 cess, wherein the cooling in (f) is carried out for a duration in the range of from 2 to 24 h, preferably in the range of from 6 to 12 h.

A further preferred embodiment (74) concretizing any one of embodiments (30) to (43) relates to
30 said process, wherein the process comprises after (a) and prior to (c) as defined in embodiment (30),

(a') heating the reaction mixture obtained in (a) in a gas atmosphere having a temperature in the range of from 60 to 100 °C, preferably in the range of from 75 to 85 °C;

(a'') admixing a source of a support material to the reaction mixture obtained from (a'), wherein the process preferably does not comprise (b).

35 A further preferred embodiment (75) concretizing embodiment (74) relates to said process, wherein the gas atmosphere in (a'), comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

40 A further preferred embodiment (76) concretizing embodiment (74) or (75) relates to said process, wherein the reaction mixture obtained in (a'') exhibits a molar ratio of the source of a support material to Nb, support material:Nb, in the range of from 1:1 to 100:1, preferably in the range of from 5:1 to 45:1, more preferably in the range of from 7:1 to 42:1.

A further preferred embodiment (77) concretizing any one of embodiments (74) to (76) relates to said process, wherein the reaction mixture obtained in (a'') exhibits a molar ratio of the source of a support material to V, support material:V, in the range of from 1:1 to 50:1, preferably in the range of from 2:1 to 25:1, more preferably in the range of from 4:1 to 18:1.

A further preferred embodiment (78) concretizing any one of embodiments (74) to (77) relates to said process, wherein the reaction mixture obtained in (a'') exhibits a molar ratio of the source of a support material to P, support material:P, in the range of from 0.1:1 to 25:1, preferably in the range of from 1:1 to 10:1, more preferably in the range of from 2:1 to 6:1.

A further preferred embodiment (79) concretizing any one of embodiments (74) to (78) relates to said process, wherein the support material is selected from the group consisting of silica, alumina, silica-alumina, titania, silica-titania, alumina-titania, silica-alumina-titania, and a mixture of two or more thereof, wherein the support material preferably comprises, more preferably consists of, silica.

A further preferred embodiment (80) concretizing any one of embodiments (74) to (79) relates to said process, wherein the thermal treatment in (c) comprises heating the reaction mixture obtained in (a'') or the dried reaction mixture obtained in (b), preferably the reaction mixture obtained in (a''), to a temperature in the range of from 60 to 100 °C, preferably in the range of from 70 to 90 °C, more preferably in the range of from 75 to 85 °C.

A further preferred embodiment (81) concretizing any one of embodiments (74) to (80) relates to said process, wherein the thermal treatment in (c) comprises heating the reaction mixture obtained in (a'') or the dried reaction mixture obtained in (b), preferably the reaction mixture obtained in (a''), for a duration in the range of from 5 to 30 h, preferably in the range of from 12 to 20 h, more preferably in the range of from 15 to 17 h.

A further preferred embodiment (82) concretizing any one of embodiments (74) to (81) relates to said process, wherein tempering in (d) comprises, preferably consists of,

(d.1) subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature in the range of from 300 to 500 °C, preferably in the range of from 350 to 450 °C;

(d.2) optionally subjecting the precursor of the mixed oxide obtained in (d.1) to a heat treatment in a gas atmosphere having a temperature in the range of from 400 to 600 °C, preferably in the range of from 450 to 550 °C;

(d.3) optionally subjecting the precursor of the mixed oxide obtained in (d.1) or (d.2) to a heat treatment in a gas atmosphere having a temperature in the range of from 500 to 700 °C, preferably in the range of from 550 to 650 °C;

(d.4) optionally subjecting the precursor of the mixed oxide obtained in (d.1), (d.2) or (d.3) to a heat treatment in a gas atmosphere having a temperature in the range of from 600 to 800 °C, preferably in the range of from 650 to 750 °C.

A further preferred embodiment (83) concretizing any one of embodiments (74) to (82) relates to said process, wherein the heat treatment in any one of (d.1), (d.2), (d.3), and (d.4) as defined in embodiment (82), independently from one another, is carried out for a duration in the range of
5 from 10 h to 40 d, preferably in the range of from 20 h to 28 d, more preferably in the range of from 23 h to 25 d.

A further preferred embodiment (84) concretizing any one of embodiments (74) to (83) relates to said process, wherein the gas atmosphere in any one of (d.1), (d.2), (d.3), and (d.4) as defined
10 in embodiment (82) or (83), independently from one another, comprises one or more of air, dry air, nitrogen, argon, and a mixture of two or more thereof.

A further preferred embodiment (85) concretizing any one of embodiments (30) to (84) relates to said process, wherein the process further comprises
15 (e) subjecting the mixed oxide obtained in (d) to a heat treatment in a gas atmosphere having a temperature in the range of from 650 to 750 °C, preferably in the range of from 690 to 710 °C.

A further preferred embodiment (86) concretizing embodiment (85) relates to said process,
20 wherein the heat treatment in (e) is carried out for a duration in the range of from 0.5 to 7 d, preferably in the range of from 1 to 5 d, more preferably in the range of from 2 to 4 d.

An embodiment (87) of the present invention relates to a mixed oxide, preferably a mixed oxide according to any one of embodiments (1) to (29), obtainable or obtained by a process according
25 to any one of embodiments (30) to (86).

An embodiment (88) of the present invention relates to a mixed oxide supported on a support material, preferably a mixed oxide according to any one of embodiments (1) to (29) supported
30 on a support material, obtainable or obtained by a process according to any one of embodiments (74) to (86), preferably according to any one of embodiments (74) to (84).

An embodiment (88) of the present invention relates to a molding, comprising a mixed oxide according to any one of embodiments (1) to (29) and (87) to (88) and an oxidic binder.

A preferred embodiment (89) concretizing embodiment (88) relates to said molding, wherein the molding comprises the oxidic binder, calculated as the respective oxide, in an amount in the
35 range of from 2 to 90 weight-%, more preferably in the range of from 5 to 70 weight-%, more preferably in the range of from 10 to 50 weight-%, more preferably in the range of from 15 to 30 weight-%, based on the total weight of the molding.

A further preferred embodiment (91) concretizing embodiment (89) or (90) relates to said molding,
40 wherein the oxidic binder preferably comprises one or more of zirconia, alumina, titania,

silica and a mixed oxide comprising two or more of Zr, Al, Ti and Si, wherein the oxidic binder more preferably comprises one or more of alumina and silica, more preferably silica.

5 A further preferred embodiment (92) concretizing any one of embodiments (89) to (91) relates to said molding, wherein the molding is in the form of a tablet or an extrudate.

10 An embodiment (93) of the present invention relates to a use of a mixed oxide according to any one of embodiments (1) to (29) and (87) to (88), or of a molding according to any one of embodiments (89) to (92), as a catalyst or a catalyst component, preferably in a reaction for converting
one or more hydrocarbons, preferably in an oxidation reaction, of one or more hydrocarbons, more preferably in a selective partial oxidation of one or more hydrocarbons, preferably substituted hydrocarbons, wherein the hydrocarbons preferably comprise, more preferably consist of,
15 an alkane, an alkene, an aldehyde, a ketone, or an aromatic, wherein the hydrocarbons more preferably are selected from the group consisting of propanol, isopropanol, propionaldehyde, butanol, butyraldehyde, benzene, toluene, xylene, acrolein, methacrolein, ethane, ethylene, propane, propene, n-butane, but-1-ene, but-2-ene, isobutylene, 1,3-butadiene, isobutane, n-pentane, 1-pentene, 2-methyl-but-1-ene, 2-methyl-but-2-ene, 3-methyl-but-1-ene, and a mixture
20 of two or more thereof, more preferably from the group consisting of ethane, ethylene, propane, propene, n-butane, but-1-ene, but-2-ene, isobutylene, 1,3-butadiene, isobutane, n-pentane, 1-pentene, 2-methyl-but-1-ene, 2-methyl-but-2-ene, 3-methyl-but-1-ene, and a mixture of two or more thereof, more preferably from the group consisting of propane, propene, n-butane, but-1-ene, but-2-ene, isobutylene, 1,3-butadiene, isobutane, and a mixture of two or more thereof, more preferably from the group consisting of propane, propene, n-butane, but-1-ene, but-2-ene, 1,3-butadiene, , and a mixture of two or more thereof, more preferably selected from the group
25 consisting of propane, propene, n-butane, and a mixture of two or more thereof.

An embodiment (94) of the present invention relates to a process for the oxidation, preferably for the partial oxidation, more preferably for the selective partial oxidation, of one or more hydrocarbons, the process comprising

- 30 (A) providing a reactor comprising a reaction zone, wherein the reaction zone comprises a catalyst, said catalyst comprising a mixed oxide according to any one of embodiments (1) to (29) and (87) to (88) or a molding according to any one of embodiments (89) to (92);
(B) introducing a reaction gas stream in the reaction zone according to (A), wherein the reaction gas stream comprises the one or more hydrocarbons, oxygen (O₂), water (H₂O) and
35 preferably one or more inert gases;
(C) subjecting the reaction gas stream to oxidation conditions in the reaction zone according to (A);
(D) separating a product gas stream from the reaction zone, wherein the product gas stream comprises at least one oxidation product of the one or more hydrocarbons.

40 A preferred embodiment (95) concretizing embodiment (94) relates to said process, wherein the reaction zone comprises the mixed oxide or the molding in a fixed-bed.

A further preferred embodiment (96) concretizing embodiment (94) or (95) relates to said process, wherein the reactor comprises two or more reaction zones.

5 A further preferred embodiment (97) concretizing embodiment (96) relates to said process, wherein the two or more reaction zones are arranged in parallel to each other.

A further preferred embodiment (98) concretizing embodiment (96) or (97) relates to said process, wherein the two or more reaction zones are serially arranged.

10 A further preferred embodiment (99) concretizing any one of embodiments (94) to (98) relates to said process, wherein the mixed oxide is comprised in a molding, preferably in the molding according to (A).

15 A further preferred embodiment (100) concretizing any one of embodiments (94) to (99) relates to said process, wherein the mixed oxide or the molding is heated in (A) to a temperature in the range of from 150 to 350 °C, preferably in the range of from 170 to 330 °C, more preferably in the range of from 180 to 320 °C, more preferably in the range of from 190 to 310 °C.

20 A further preferred embodiment (101) concretizing any one of embodiments (94) to (100) relates to said process, wherein the mixed oxide or the molding is heated in (B) to a temperature in the range of from 350 to 500 °C, preferably in the range of from 370 to 480 °C, more preferably in the range of from 380 to 470 °C, more preferably in the range of from 390 to 460 °C.

25 A further preferred embodiment (102) concretizing any one of embodiments (94) to (101) relates to said process, wherein after (A) and prior to (B) the mixed oxide or the molding is heated to a temperature in the range of from 150 to 350 °C, preferably in the range of from 170 to 330 °C, more preferably in the range of from 180 to 320 °C, more preferably in the range of from 190 to 310 °C, and wherein in (B) the mixed oxide or the molding is heated to a temperature in the range of from 350 to 500 °C, preferably in the range of from 370 to 480 °C, more preferably in the range of from 380 to 470 °C, more preferably in the range of from 390 to 460 °C.

35 A further preferred embodiment (103) concretizing any one of embodiments (94) to (102) relates to said process, wherein the hydrocarbons are selected from the group consisting of propanol, isopropanol, propanal, butanol, butyraldehyde, benzene, toluene, xylene, acrolein, methacrolein, ethane, ethylene, propane, propylene, n-butane, 1-butene, 2-butene, 1,3-butadiene, isobutene, isobutene, n-pentane, 1-pentene, 2-methyl-1-butene, isopentene, 3-methyl-1-butene, and a mixture of two or more thereof, preferably selected from the group consisting of ethane, ethylene, propane, propylene, n-butane, 1-butene, 2-butene, 1,3-butadiene, isobutane, isobutene, n-pentane, 1-pentene, 2-methyl-1-butene, isopentene, 3-methyl-1-butene, and a mixture of two or more thereof, more preferably selected from the group consisting of propane, propylene, n-butane, 1-butene, 2-butene, 1,3-butadiene, isobutane, isobutene, and a mixture of two or more thereof, more preferably selected from the group consisting of propane, propylene, n-butane, 1-butene, 2-butene, 1,3-butadiene, and a mixture of two or more thereof, more preferably selected

from the group consisting of propane, propylene, n-butane, and a mixture of two or more thereof.

A further preferred embodiment (104) concretizing any one of embodiments (94) to (103) relates to said process, wherein the reaction gas stream in (B) exhibits a volume ratio of the one or more hydrocarbons to oxygen (O₂) in the range of from 1:1 to 1:50, preferably in the range of from 1:2 to 1:35, more preferably in the range of from 1:3 to 1:31, more preferably in the range of from 1:4 to 1:20, more preferably in the range of from 1:7 to 1:18, more preferably in the range of from 1:9 to 1:16.

A further preferred embodiment (105) concretizing any one of embodiments (94) to (104) relates to said process, wherein the reaction gas stream in (B) exhibits a volume ratio of the one or more hydrocarbons to water (H₂O) in the range of from 10:1 to 1:25, preferably in the range of from 5:1 to 1:20, more preferably in the range of from 2:1 to 1:10, more preferably in the range of from 1:1 to 1:5, more preferably in the range of from 1:2 to 1:4.

A further preferred embodiment (106) concretizing any one of embodiments (94) to (105) relates to said process, wherein from 95 to 100 volume-%, preferably from 97 to 100 volume-%, more preferably from 98 to 100 volume-%, more preferably from 99 to 100 volume-%, of the reaction gas stream introduced in (B) in the reaction zone consists of one or more hydrocarbons, oxygen (O₂), water (H₂O) and one or more inert gases.

A further preferred embodiment (107) concretizing any one of embodiments (94) to (106) relates to said process, wherein the reaction gas stream in (B) comprises from 0.1 to 5.0 volume-% of hydrocarbons, preferably from 0.3 to 3.5 volume-%, more preferably from 0.5 to 2.5 volume-%, more preferably from 0.75 to 2.25 volume-%, more preferably from 0.9 to 2.1 volume-%.

A further preferred embodiment (108) concretizing any one of embodiments (94) to (107) relates to said process, wherein the reaction gas stream in (B) comprises from 5 to 25 volume-% of oxygen (O₂), preferably from 10 to 25 volume-%, more preferably from 12 to 23 volume-%, more preferably from 14 to 21 volume-%.

A further preferred embodiment (109) concretizing any one of embodiments (94) to (108) relates to said process, wherein the reaction gas stream in (B) comprises from 0.1 to 25 volume-% of water (H₂O), preferably from 0.5 to 20 volume-%, more preferably from 0.75 to 10 volume-%, more preferably from 1 to 5 volume-%, more preferably from 2.5 to 3.5 volume-%.

A further preferred embodiment (110) concretizing any one of embodiments (94) to (109) relates to said process, wherein the oxidation conditions in the reaction zone comprise a pressure in the range of from 0.5 to 5 bar(abs), preferably in the range of from 0.6 to 4 bar(abs), more preferably in the range of from 0.7 to 3.5 bar(abs), more preferably in the range of from 0.9 to 3.1 bar(abs).

A further preferred embodiment (111) concretizing any one of embodiments (94) to (110) relates to said process, wherein the oxidation conditions in the reaction zone comprise gas hourly space velocity of the reaction gas stream based on the volume of the mixed oxide provided in (A) in the range of from 300 to 100 000 h⁻¹, preferably in the range of from 1 000 to 10 000 h⁻¹,
5 more preferably in the range of from 1 500 to 6 000 h⁻¹.

A further preferred embodiment (112) concretizing any one of embodiments (94) to (111) relates to said process, wherein the inert gases comprise nitrogen (N₂), argon, or a mixture thereof, preferably nitrogen (N₂) and argon, wherein the inert gases more preferably consist of nitrogen
10 (N₂) and argon.

A further preferred embodiment (113) concretizing any one of embodiments (94) to (112) relates to said process, wherein from 95 to 100 volume-%, preferably from 96 to 100 volume-%, more preferably from 98 to 100 volume-%, more preferably from 99 to 100 volume-%, of the inert
15 gases consists of nitrogen (N₂) and argon.

A further preferred embodiment (114) concretizing any one of embodiments (94) to (113) relates to said process, wherein from 1 to 5 volume-%, preferably from 2 to 4 volume-%, of the inert
20 gases comprise, preferably consist of, argon.

A further preferred embodiment (115) concretizing any one of embodiments (94) to (114) relates to said process, wherein the oxidation conditions are isothermal.

A further preferred embodiment (116) concretizing any one of embodiments (94) to (115) relates
25 to said process, wherein the reaction gas stream comprises propane or propylene and the product gas stream comprises acrolein, acrylic acid or a mixture thereof.

A further preferred embodiment (117) concretizing any one of embodiments (94) to (116) relates
30 to said process, wherein the reaction gas stream comprises n-butane and the product gas stream comprises maleic anhydride.

The present invention is further illustrated by the following examples and reference examples.

EXAMPLES

5 Reference Example 1: Determination of powder X-ray diffraction and of crystalline and amorphous phases

Powder diffraction patterns were recorded with an IP Guinier-Camera G670 (Huber company, Germany) and a Bragg-Brentano Diffractometer D8 Advanced (Bruker AXS) and Cu-Kalpha1
10 radiation ($\lambda = 1.54059$ Angstrom). Lattice parameters were determined manually or with the software package S.O.S. (Literature: J. Soose, G. Meyer, SOS – Programme zur Auswertung von Guinier-Aufnahmen (engl. "SOS – programs for evaluating Guinier recordings"); University of Gießen, Germany 1980).

15 To determine the amount of crystalline and amorphous phases in a powder sample a standard addition method is used, where a known amount of a standard is added to a decent amount of the powder sample. Typical standards used are quartz (SiO_2), yttrium oxide (Y_2O_3) or corundum (Al_2O_3). The amounts of crystalline phases and the respective added standard are determined within a quantitative phase analysis (QPA) with common Rietveld refinement programs
20 (TOPAS, Fullprof, etc.). Based on the QPA the relative mass fractions of crystalline phases/ analyte (W_i) are calculated and converted to absolute mass fractions ($W_{i,abs.}$) with equation (I). The amount of amorphous phase is derived from the overall amount (100 %) minus the sum of crystalline phases according to equation (II).

$$25 \quad W_{i,abs.} = W_i \cdot \frac{S_{abs.}}{S_i} \quad (I)$$

$S_{abs.}$ = Rietveld scale factor of the analyte

S_i = Rietveld scale factor of the standard

$$30 \quad W_{amorph} = 1 - \sum_{i=1}^m W_i \quad (II)$$

Literature: Ian C. Madsen, Nicola V. Y. Scarlett and Arnt Kern, Z. Kristallogr. 2011, 226, 944.

35 Reference Example 2: Determination of the elemental composition of a mixed oxide

The elemental composition of a mixed oxide was determined via X-ray fluorescent spectroscopy with a M4 Tornado spectrometer from Bruker utilizing a Rh microfocus X-ray tube (25 micrometer). For a sample, 50 datapoints were measured and evaluated with the ESPRIT M4 Tornado software package.

40

Reference Example 3: Determination of the BET specific surface area

The BET specific surface area was determined via nitrogen physisorption at 77 K according to the method disclosed in DIN 66131.

5 **Reference Example 4: Providing a source of a support material**

The silica (Q20C from Fujisilysia; average pore diameter of 20 nm; pore volume of 0.80 ml/g; surface area of 140 m²/g; bulk density of 0.55 g/ml) used as a source for the support material was crushed in a centrifugal mill (centrifugal mill Retsch ZM 200; 2 mm sieve insert; 6000
10 U/min). The resulting split was sieved with a sieve set to obtain fractions with sieve inserts having a diameter of 200 µm. The sieve set had the following bottom-up assembly: bottom, 500 micrometer sieve, 1000 micrometer sieve. The solids obtained from milling were sieved with the sieve set using a sieving apparatus (sieving apparatus Retsch AS 200, 70 Hz, 10 min). The target sieve fraction was obtained between the sieves of 500 micrometer and 1000 micrometer.
15 The other fractions smaller than 500 micrometer and greater than 1000 micrometer were separated.

20 **Examples 1-3: Preparation of mixed oxides via solution combustion synthesis (SCS)**

Three different mixed oxides were prepared via solution combustion synthesis according to the following general description whereby the used amounts of starting materials are listed in table 1 below. The prepared mixed oxides comprised Nb and V but differed in particular in their Nb:V molar ratio. The mixed oxide of Example 1 has the empirical formula (V_{0.7}Nb_{0.3})OPO₄, Example
25 2 comprised a mixed oxide having the empirical formula (V_{0.5}Nb_{0.5})OPO₄ and Example 3 comprised a mixed oxide having the empirical formula (V_{0.3}Nb_{0.7})OPO₄.

A solution of ammonium metavanadate (NH₄VO₃), ammonium niobate(V) oxalate hydrate (NH₄NbO(C₂O₄)₂ · 7.9 H₂O), and diammonium hydrogen phosphate ((NH₄)₂HPO₄) were dissolved in a beaker in 100 ml de-ionized water. Glycine was then added thereto in a molar
30 amount approximately three-times of the molar amount of V.

Subsequently, 2 ml of nitric acid were added, and the resulting mixture is dried overnight under stirring using a Teflon-coated bar in air at a temperature of 70 °C to dryness thus obtaining a
35 gel-like reaction mixture.

The reaction mixture in the beaker was then ignited in a chamber furnace having a temperature of 400 °C. Heating was continued for further 10 min for completing the solution combustion synthesis. As a result from the thermal decomposition of the reaction mixture a black powder was
40 obtained as an amorphous precursor of the mixed oxide. The powder was ground in a mortar and then subjected to tempering for a total time of four days, wherein tempering was performed one day in air at a temperature of 400 °C, then one day in air at a temperature of 500 °C, then one day in air at a temperature of 600 °C, and finally one day in air at a temperature of 700 °C.

The resulting mixed oxide had a lemon-yellow appearance in color. Tempering in air at a temperature of 700 °C may be continued for obtaining a higher crystallinity of the mixed oxide. The BET specific surface area was determined according to Reference Example 3 for a mixed oxide of Example 1 as being in the range of from 3 to 6 m²/g and for a mixed oxide of Example 3 as being in the range of from 35 to 47 m²/g.

Table 1

Starting materials and used amounts thereof for the preparation of Examples 1-3

#	Starting materials	Amount
Example 1 (V _{0.3} Nb _{0.15})P _{0.5} O _{2.5}	NH ₄ VO ₃ NH ₄ NbO(C ₂ O ₄) ₂ · 7.9 H ₂ O (NH ₄) ₂ HPO ₄ HNO ₃ Glycine	938.47 mg (8.023 mmol) 1532.29 mg (3.438 mmol) 1513.52 mg (11.462 mmol) 2 ml 1870 mg (25 mmol)
Example 2 (V _{0.25} Nb _{0.25})P _{0.5} O _{2.5}	NH ₄ VO ₃ NH ₄ NbO(C ₂ O ₄) ₂ · 7.9 H ₂ O (NH ₄) ₂ HPO ₄ HNO ₃ Glycine	639.55 mg (5.468 mmol) 2436.27 mg (5.467 mmol) 1444.07 mg (10.936 mmol) 2 ml 1260 mg (17 mmol)
Example 3 (V _{0.15} Nb _{0.35})P _{0.5} O _{2.5}	NH ₄ VO ₃ NH ₄ NbO(C ₂ O ₄) ₂ · 7.9 H ₂ O (NH ₄) ₂ HPO ₄ HNO ₃ Glycine	366.89 mg (3.237 mmol) 3261.63 mg (7.319 mmol) 1393.66 mg (10.554 mmol) 2 ml 848 mg (11 mmol)

Examples 4-5: Preparation of mixed oxides via hydrothermal synthesis

Two different mixed oxides were prepared via hydrothermal synthesis according to the following general description whereby the used amounts of starting materials are listed in table 2 below.

The prepared mixed oxides comprised Nb and V but differed in particular in their Nb:V molar ratio. Example 4 comprised a mixed oxide having the empirical formula V_{0.05}Nb_{0.45}P_{0.5}O_{2.5}, and Example 5 comprised a mixed oxide having the empirical formula V_{0.15}Nb_{0.35}P_{0.5}O_{2.5}.

An aqueous solution of ammonium niobate(V) oxalate hydrate (NH₄NbO(C₂O₄)₂ · 7.9 H₂O; 0.45 mol/l), was mixed with ammonium metavanadate (NH₄VO₃) and phosphoric acid (85 % in water). The obtained reaction mixture was put in an autoclave and sealed (250 ml autoclave of Berghof GmbH). Then, the reaction mixture was heated with a heating rate of 100°C/h to a temperature of 200 °C. Said temperature was hold for 48 h whereby the reaction mixture was stirred at 500 rpm. After that, the reaction mixture was filtrated and the resulting solids were subjected to tempering for 12 h in air at a temperature of 400 °C, then for 24 h in air at a temperature of 500 °C, and finally for 24 h in air at a temperature of 600 °C, to obtain a mixed ox-

ide. The BET specific surface area was determined according to Reference Example 3 for mixed oxides of Examples 4 and 5 as being 10 m²/g.

Table 2

5 Starting materials and used amounts thereof for the preparation of Examples 4-5

#	V (H ₃ PO ₄) [ml]	m (NH ₄ VO ₃) [g]	m (NH ₄ NbO(C ₂ O ₄) ₂ · 7.9 H ₂ O) [g]
Example 4 V _{0.05} Nb _{0.45} P _{0.5} O _{2.5}	1.028	0.240	6.281
Example 5 V _{0.15} Nb _{0.35} P _{0.5} O _{2.5}	1.160	0.813	5.516

Examples 6-8: Preparation of mixed oxides supported on a support material via incipient wetness synthesis

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Three different mixed oxides were prepared via incipient wetness synthesis according to the following general description whereby the used amounts of starting materials are listed in table 3 below. The prepared mixed oxides comprised Nb and V but differed in particular in their Nb:V molar ratio. Example 6 comprised a mixed oxide having the empirical formula (V_{0.9}Nb_{0.1})OPO₄

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V_{0.45}Nb_{0.05}P_{0.5}O_{2.5}, Example 7 comprised a mixed oxide having the empirical formula V_{0.35}Nb_{0.15}P_{0.5}O_{2.5}, and Example 8 comprised a mixed oxide having the empirical formula V_{0.15}Nb_{0.35}P_{0.5}O_{2.5}.

20

As a support material a silica was used (silica Q20C from Fujisilysia having the following characteristics according to fujisilysia.com: 20 nm average pore diameter, 0.80 ml/g pore volume, 140 m²/g surface area, 0.55 g/ml bulk density). As starting materials, deionized water, phosphoric acid (85 weight-% in water), vanadyl sulfate (VOSO₄ · x H₂O, wherein x is in the range of from 2.80 to 2.85), and ammonium niobate(V) oxalate hydrate (NH₄NbO(C₂O₄)₂ · 7.9 H₂O) were used.

25

According to the amounts given in table 3, an aqueous solution comprising de-ionized water, vanadyl sulfate hydrate and ammonium niobate(V) oxalate hydrate was prepared. Phosphoric acid was then added to said solution and the resulting suspension heated to a temperature of 80 °C for obtaining a solution. Then, the silica was added to the aqueous solution for impregnation thereof. To this effect, the resulting mixture was dried in air for 16 h under stirring. The resulting solids were sieved and the fraction having a particle size of 500 to 1000 micrometer was separated. Said separated fraction was then subjected to tempering in air at a temperature of 450 °C for 12 h, whereby a heating rate of 5 K/min was applied.

35

Table 3

Starting materials and used amounts thereof for the preparation of Examples 6-8

#	V (H ₂ O) [ml]	V (H ₃ PO ₄)	m (silica) [g]	m (VOSO ₄ · x H ₂ O, 2.80 ≤ x ≤ 2.85)	m (NH ₄ NbO(C ₂ O ₄) ₂ · 7.9 H ₂ O)
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		[ml]		[g]	[g]
Example 6 $V_{0.45}Nb_{0.05}P_{0.5}O_{2.5}$	40.0	1.1919	3.0	2.3353	0.5402
Example 7 $V_{0.35}Nb_{0.15}P_{0.5}O_{2.5}$	40.0	1.0861	3.0	1.6550	1.4766
Example 8 $V_{0.15}Nb_{0.35}P_{0.5}O_{2.5}$	40.0	0.9222	3.0	0.6023	2.9257

Example 9: Characterization of the prepared mixed oxides of Examples 1-8

5 The prepared mixed oxides according to Examples 1-8 were characterized by powder X-ray diffraction according to Reference Example 1. It was found that each of the Examples 1-5 had a crystallinity of higher than 90 % and comprised an alpha(II) $VOPO_4$ crystalline phase and an alpha $NbOPO_4$ crystalline phase. A powder X-ray diffraction pattern of the mixed oxide according to Example 5 comprising a mixed oxide having the empirical formula $V_{0.15}Nb_{0.35}P_{0.5}O_{2.5}$ is shown in Figure 1. A simulated X-ray diffraction pattern of the alpha $NbOPO_4$ crystalline phase is also shown in Figure 1. Simulated X-ray diffraction patterns were prepared based on xy-files (d vs. I) from XRD using Bragg's law. None of the mixed oxides according to Examples 1-9 comprised a vanadyl pyrophosphate crystalline phase. Further, no pure Vegards behavior was observed for the examples.

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Example 10: Catalytic testing of the prepared mixed oxides in the partial oxidation of n-butane to maleic anhydride (MAN)

20 The catalytic oxidation of n-butane was tested using mixed oxides according to Examples 3, 5, and 8 in high throughput tests with a reactor set up of eight parallel reactors each loaded with a sample of a mixed oxide.

25 The yields of maleic anhydride, carbon monoxide and carbon dioxide were determined depending on the conversion of used n-butane. Further, the selectivities towards said compounds were also determined depending on the conversion of used n-butane. In the tested oxidation reaction by-products were obtained in very low yields, inter alia butene, propionic acid, acrolein, acetaldehyde, propane, acetylene, ethene, ethane, acetic acid, 2,5-dihydrofuran, and acrylic acid.

30 For start-up, the reactors were heated under an atmosphere of nitrogen and oxygen to 300 °C. Then, n-butane, steam and argon were introduced in the reactors. Said gas streams formed a reaction gas stream for each of the reactors, wherein each reaction gas stream comprised 2 volume-% n-butane, 20 volume-% oxygen, 3 volume-% water, 2 volume-% argon, and 73 volume-% nitrogen. The flow rate of each reaction gas stream was 33.3 ml per minute. The gas
35 hourly space velocity based on the volume of the used mixed oxide was 2000 per hour whereby

a pressure of 1 bar(abs) was applied in the reaction zone. The reactors were then heated to 350 °C and said temperature was hold for 16 h before starting measurements while stepwise increasing the temperature. The temperature was increased with steps of 25 °C up to 450 °C. The phase where the temperature was increased was the “ramp-up” phase. Further measurements were recorded while cooling down, whereby cooling down was performed while cooling the temperature with steps of 25 °C until a temperature of 350 °C was reached. The cooling down phase was the “ramp-down” phase. For reactor shut-down, further cooling was performed with nitrogen and oxygen to cool down to room temperature. The gas streams exiting the reactors were analyzed gas chromatographically to determine the yields and selectivities. The carbon balance was $100 \pm 3 \%$. For low conversions of n-butane both product-based formulas (VI) and (VII) were considered for calculating the conversion as well as the selectivities. The conversion of n-butane X (see formulas (IV) and (VI)) and of the selectivities of the respective products S (see formulas (V) and (VII)) were calculated based on the concentrations, wherein they have been referenced against argon as internal standard. In doing so, the selectivities were averaged over five test runs at each temperature measurement point. The selectivities relating to the products and by-products (see formula (V)) were normalized with respect to the total number of carbon atoms of the product and by-product, respectively. The yield of a product Y was calculated according to formula (VIII).

The conversion of n-butane X(n-butane) was calculated according to formula (IV):

$$(IV) \quad X(\text{n-butane}) = 1 - (C_{\text{n-butane}} / C_{\text{n-butane},0}) * (C_{\text{Ar},0} / C_{\text{Ar}}),$$

wherein $C_{\text{n-butane}}$ represents the concentration of n-butane in the outlet gas stream, $C_{\text{n-butane},0}$ the concentration of n-butane in the inlet (reaction) gas stream, $C_{\text{Ar},0}$ the concentration of argon in the inlet (reaction) gas stream and C_{Ar} the concentration of argon in the outlet gas stream.

The selectivity towards a product i S_i was calculated according to formula (V):

$$(V) \quad S_i = c_i * C_{\text{Ar},0} * N_{\text{C},i} / 4 * ((C_{\text{n-butane},0} * C_{\text{Ar}}) - (C_{\text{n-butane}} * C_{\text{Ar},0}))$$

wherein c_i represents the concentration of product i, $C_{\text{Ar},0}$ the concentration of argon in the inlet (reaction) gas stream, C_{Ar} the concentration of argon in the outlet gas stream, $N_{\text{C},i}$ the total number of carbon atoms of the product, $C_{\text{n-butane}}$ the concentration of n-butane in the outlet gas stream and $C_{\text{n-butane},0}$ the concentration of n-butane in the inlet (reaction) gas stream.

For low conversions of n-butane the conversion was calculated according to the product-based formula (VI):

$$(VI) \quad X(\text{n-butane}) = 1 - C_{\text{n-butane}} * C_{\text{Ar},0} / (\sum C_{\text{n-butane}} + C_{\text{products}}) * C_{\text{Ar}}$$

For low conversions of n-butane the selectivity towards a product i S_i was calculated according to product-based formula (VII):

$$(VII) \quad S_i = c_i * c_{Ar,0} * N_{c,i} / (4 * (\sum C_{n-butane} + C_{products}) * C_{Ar} - C_{n-butane} * C_{Ar,0})$$

The yield of a product Y_i was calculated according to formula (VIII):

$$(VIII) \quad Y_i = X * S_i$$

5

Figure 2 shows the results from catalytic testing of the prepared mixed oxides according to Examples 3, 5, and 8 in the partial oxidation of n-butane to maleic anhydride (MAN). The selectivity towards maleic anhydride S_{MAN} is shown on the ordinate in % and the conversion of n-butane $X_{n-butane}$ is shown on the abscissa in % for Example 3 (open and filled circles), Example 5 (open and filled left facing triangles), and Example 8 (open and filled triangles). Open circles and triangles indicate values recorded while the temperature was decreasing, thus during ramp-down phase, and filled symbols indicate values recorded while the temperature was increasing, thus during ramp-up phase.

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It can be taken from the results of catalytic testing that the mixed oxides according to Examples 3, 5, and 8 show good catalytic activity. In particular, the mixed oxide of Example 3 shows the best catalytic activity since a selectivity towards maleic anhydride was achieved in the range about 20 to 30 % even at higher conversion rates of n-butane. In sum, all tested examples showed a good catalytic activity in the catalytic conversion of n-butane to maleic anhydride.

20

Example 11: Catalytic testing of the prepared mixed oxides in the oxidation of propane

The catalytic oxidation of propane was tested using mixed oxides according to Examples 4 and 5 in high throughput tests with a reactor set up of 48 parallel reactors each loaded with a sample of a mixed oxide.

25

The yield of propylene was determined depending on the conversion of used propane. Further, the selectivity towards propylene was also determined depending on the conversion of used propane. In the tested oxidation reaction by-products were obtained in very low yields, inter alia acetaldehyde, acetone, ethylene, propionic aldehyde, propionic acid, and methane.

30

For start-up, the reactors were heated under an atmosphere of nitrogen to 200 °C. Then, an argon gas stream was introduced in the reactors. After 15 min, a steam gas stream was added, after further 15 min, an oxygen (O₂) gas stream, and after further 15 min a propane gas stream. Said gas streams formed a reaction gas stream for each of the reactors, wherein each reaction gas stream comprised 1 volume-% propane, 15 volume-% oxygen, 3 volume-% water, 3 volume-% argon, and 78 volume-% nitrogen. The flow rate of each reaction gas stream was 50.5 ml per minute. The gas hourly space velocity based on the volume of the used mixed oxide was 3000 per hour whereby a pressure of 3 bar(abs) was applied in the reaction zone. The temperature of 200 °C of the reactors was held for 30 min before starting measurements while stepwise increasing the temperature. The temperature was increased with steps of 50 °C up to 400 °C,

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whereby also steps of 10 °C or 15 °C were applied for obtained more detailed measurements in temperature ranges of interest. For reactor shut-down, said steps were performed in reverse order, whereby at last cooling was performed with nitrogen to cool down to room temperature. The gas streams exiting the reactors were analyzed gas chromatographically to determine the yields and selectivities.

The conversion X of propane X(propane) was calculated according to formula (I):

$$(I) \quad X(\text{propane}) = (1 - (RC_{\text{propane}} / RC_{\text{propane-in}})) * 100,$$

wherein RC_{propane} represents the outlet flow rate of propane in g(propane)/h und $RC_{\text{propane-in}}$ the inlet flow rate of propane in g(propane)/h.

The yield Y of a product was calculated according to formula (II):

$$(II) \quad Y = (c / RC_{\text{propane-in}}) * 100,$$

wherein c represents the concentration of product in the outlet gas stream and

$RC_{\text{propane-in}}$ the inlet flow rate of propane in g(propane)/h.

The selectivity towards a product was calculated according to formula (III):

$$(III) \quad S = (c / (RC_{\text{propane-in}} - RC_{\text{propane}})) * 100,$$

wherein c represents the concentration of product in the outlet gas stream, RC_{propane} the outlet flow rate of propane in g(propane)/h and

$RC_{\text{propane-in}}$ the inlet flow rate of propane in g(propane)/h.

A flow rate of a compound i is given by the formula $RC_i / g(C)/h = (F_i / R_i) * F$, wherein F_i represents the peak-area of product i in the gas chromatogram, R_i the calculation factor determined via calibration, and F the determined flow rate of the gas phase.

The results from catalytic testing show that the mixed oxides according to Examples 4 and 5 are suitable catalysts for the oxidation of propane to propylene.

When comparing the results for Example 4 and 5 it can be particularly gathered that the mixed oxide according to Example 4 being comparatively niobium-rich shows a higher selectivity towards propylene where, however, the conversion of propane was lower than for the mixed oxide according to Example 5. Thus, the mixed oxide according to Example 5 showed a higher conversion of propane connected with a lower selectivity towards propylene.

Brief description of figures

Figure 1: shows a powder X-ray diffraction pattern of a mixed oxide of Example 3. Below the graph a simulated pattern is given for the alpha $NbOPO_4$ crystalline phase is given.

Figure 2: shows the results from catalytic testing of the prepared mixed oxides according to Examples 3, 5, and 8 in the partial oxidation of n-butane to maleic anhydride (MAN). The selectivity towards maleic anhydride S_{MAN} is shown on the ordinate in % and the conversion of n-butane $X_{\text{n-butane}}$ is shown on the abscissa in % for Example 3 (open and filled circles), Example 5 (open and filled left facing triangles), and Example 8 (open and filled triangles). Open circles and triangles indicate values recorded while the temperature was decreasing, thus during ramp-down phase, and filled symbols indicate values recorded while the temperature was increasing, thus during ramp-up phase.

Figure 3: shows the results from catalytic testing of the prepared mixed oxides according to Examples 4 and 5 in the partial oxidation of propane to propylene. The selectivity towards propylene S (Propylene) is shown on the ordinate in % and the conversion of propane X (Propane) is shown on the abscissa in % for Example 4 (grey squares) and Example 5 (black squares).

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Claims

1. A mixed oxide comprising Nb, V, P, and O, exhibiting a molar ratio of Nb to the sum of Nb and V, Nb:(Nb+V), of equal to or greater than 0.091:1, comprising a crystalline NbOPO₄ phase, and comprising a crystalline alpha(II) VOPO₄ phase in an amount in the range of from equal to or greater than 50 weight-%, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, determined as described in Reference Example 1.

2. The mixed oxide of claim 1, wherein the crystalline alpha(II) VOPO₄ phase exhibits an X-ray diffraction pattern comprising at least the following reflections:

Miller indices hkl (%)	Diffraction angle 2theta/° [Cu K(alpha 1)]
110	19.33 – 21.16
111	28.77 – 29.68
200	27.60 – 29.99

wherein the X-ray diffraction pattern is determined according to Reference Example 1.

3. The mixed oxide of claim 1 or 2, exhibiting a molar ratio of Nb to the sum of V, Nb, and P, Nb:(V+Nb+P), of equal to or greater than 0.1:1.

4. The mixed oxide of any one of claims 1 to 3, exhibiting a molar ratio of V to the sum of V, Nb, and P, V:(V+Nb+P), in the range of from 0.005:1 to 0.495:1.

5. The mixed oxide of any one of claims 1 to 4, wherein the crystalline NbOPO₄ phase comprises from 75 to 100 weight-% of a crystalline alpha NbOPO₄ phase, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, determined as described in Reference Example 1.

6. The mixed oxide of any one of claims 1 to 5, wherein the crystalline NbOPO₄ phase comprises from 0 to 25 weight-% of a crystalline beta NbOPO₄ phase, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, determined as described in Reference Example 1.

7. The mixed oxide of any one of claims 1 to 6, wherein from 90 to 100 weight-% of the mixed oxide consist of V, Nb, P, O, and H.

8. The mixed oxide of any one of claims 1 to 7, comprising from 0 to 10 weight-% of a crystalline (VO)₂P₂O₇ (vanadyl pyrophosphate) phase, based on the sum of the weight of Nb calculated as NbOPO₄ and of V calculated as VOPO₄, determined as described in Reference Example 1.

9. The mixed oxide of any one of claims 1 to 8, being supported on a support material.

10. A process for preparing a mixed oxide comprising Nb, V, P, and O, the process comprising
- 5 (a) providing a reaction mixture comprising a source of Nb, a source of V, a source of P, water, and optionally an oxidizing agent;
- (b) optionally drying the reaction mixture obtained in (a) in a gas atmosphere having a temperature in the range of from 50 to 100 °C, obtaining a dried reaction mixture;
- 10 (c) subjecting the reaction mixture obtained in (a) or the dried reaction mixture obtained in (b) to a thermal treatment in a gas atmosphere, obtaining a precursor of the mixed oxide;
- (d) subjecting the precursor of the mixed oxide obtained in (c) to tempering, said tempering comprising subjecting the precursor of the mixed oxide obtained in (c) to a heat treatment in a gas atmosphere having a temperature of at least 300 °C, obtaining the mixed oxide.
- 15 11. The process of claim 10, wherein the reaction mixture provided in (a) further comprises a fuel component.
12. A mixed oxide, obtainable or obtained by a process according to claim 10 or 11.
- 20 13. A molding, comprising a mixed oxide according to any one of claims 1 to 9 and 12 and an oxidic binder.
14. Use of a mixed oxide according to any one of claims 1 to 9 and 12, or of a molding according to claim 13, as a catalyst or a catalyst component.
- 25 15. A process for the oxidation of one or more hydrocarbons, the process comprising
- (A) providing a reactor comprising a reaction zone, wherein the reaction zone comprises a catalyst, said catalyst comprising a mixed oxide according to any one of claims 1 to 9 and 12 or a molding according to claim 13;
- 30 (B) introducing a reaction gas stream in the reaction zone according to (A), wherein the reaction gas stream comprises the one or more hydrocarbons, oxygen (O₂), and water (H₂O);
- (C) subjecting the reaction gas stream to oxidation conditions in the reaction zone according to (A);
- 35 (D) separating a product gas stream from the reaction zone, wherein the product gas stream comprises at least one oxidation product of the one or more hydrocarbons.

Figure 1

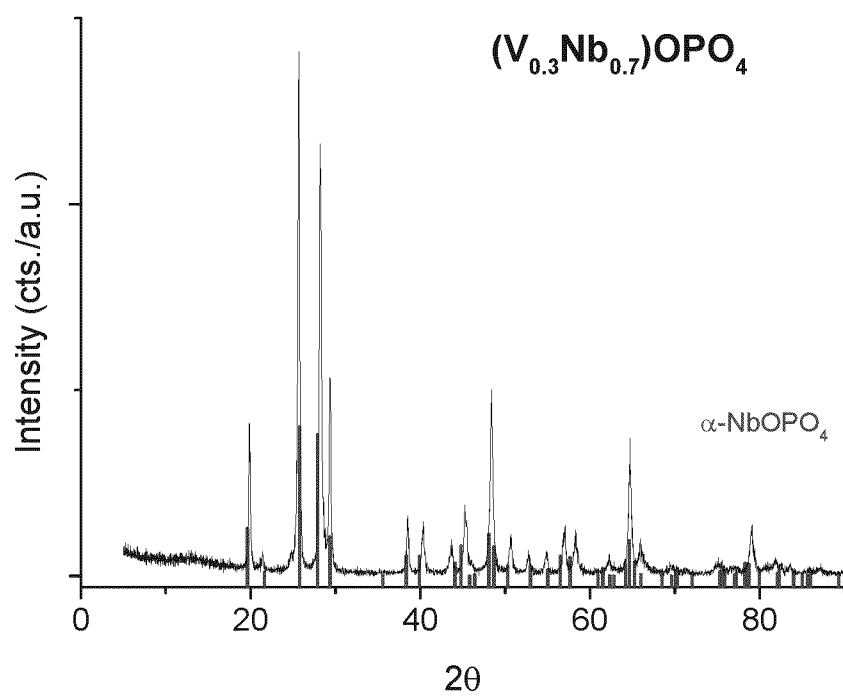


Figure 2

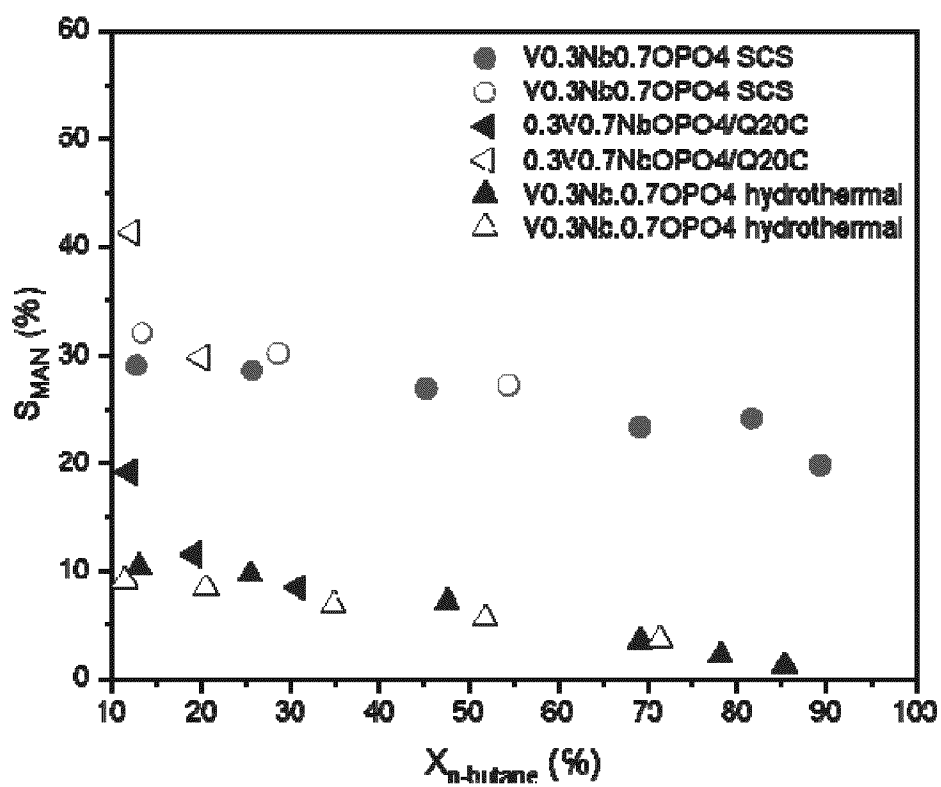
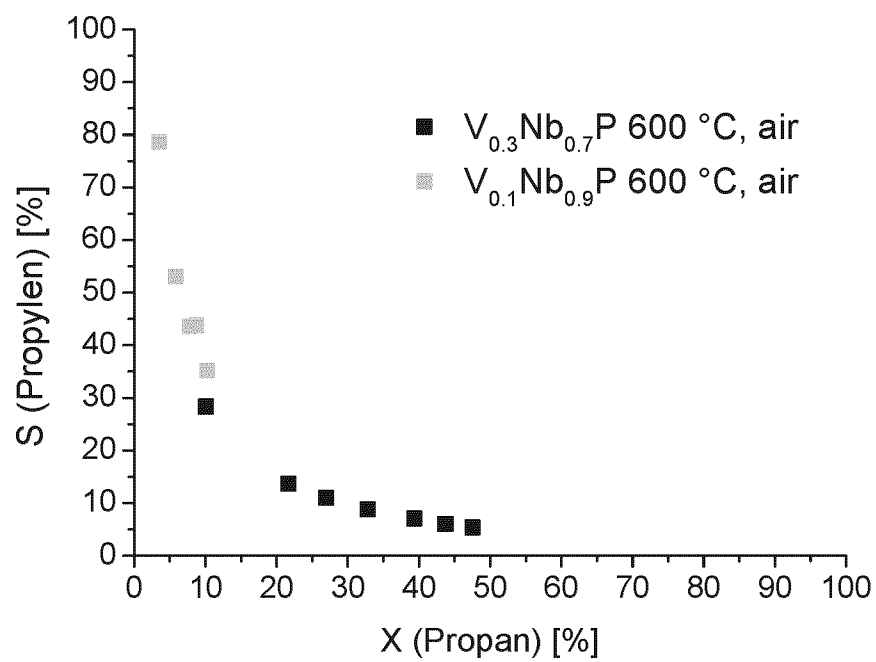


Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/073382

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J23/22 B01J27/198 C07C51/215
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MASTUURA I ET AL: "Promotional effect of niobium phosphate for vanadyl pyrophosphate catalyst on selective oxidation of butane to maleic anhydride", CATALYSIS TODAY, AMSTERDAM, NL, vol. 28, 1 January 1996 (1996-01-01), pages 133-138, XP002270181, DOI: 10.1016/0920-5861(95)00220-0 cited in the application Experimental; figures	1-15
A	----- WO 2005/025742 A1 (LONZA SPA [IT]; GHELFI FEDERICO [IT] ET AL.) 24 March 2005 (2005-03-24) cited in the application the whole document -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

15 November 2021

Date of mailing of the international search report

02/12/2021

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2021/073382

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