

Catalysts based on titanium-containing, organic-inorganic hybrid materials for the selective oxidation of hydrocarbons

5 The present invention relates to supported compositions comprising gold and/or silver particles and titanium-containing, organic-inorganic hybrid materials, a process for their preparation and their use as a catalyst for the selective oxidation of hydrocarbons. The catalytically
10 active compositions show high selectivities and productivities.

The direct oxidation of ethene to ethene oxide by molecular oxygen is well-known and is used commercially for the
15 production of ethene oxide in the gas phase. The typical catalyst for this use comprises metallic or ionic silver, possibly also modified with various promoters and activators. Most of these catalysts comprise a porous, inert catalyst support of low surface area, such as e.g.
20 alpha-aluminium oxide, on to which silver and promoters have been applied. An overview of the direct oxidation of ethene in the presence of supported silver catalysts has been compiled by Sachtler et al. in Catalysis Reviews: Science and Engineering, 23 (1&2), 127-149 (1981).

25 It is also known that these silver catalysts and the reaction conditions which have proved to be favourable for ethene oxide production do not lead to comparably good results in the direct oxidation of higher olefins, such as
30 propene (US 5 763 630, US 5 703 254 and US 5 760 254), and maximum propene oxide selectivities of approx. 50% are

achieved. In general, direct oxidations of these higher olefins with molecular oxygen in the gas phase do not proceed below 200°C - even in the presence of catalysts - and it is therefore difficult to selectively prepare oxidation-sensitive oxidation products, such as epoxides, since the secondary reactions of these products often proceed faster than the oxidation of the olefins employed itself. Another problem results from the sensitivity of the allyl groups present in higher olefins to oxidation.

For this reason, propene oxide is currently prepared in the chemical industry exclusively in the liquid phase by an indirect route.

The patent US 5 623 090 describes a gas phase direct oxidation of propene to propene oxide with relatively low propene conversions (0.5-1% propene conversion, based on a 10% propene feed concentration) but propene oxide selectivities of > 90%. This is a gas phase oxidation with molecular oxygen and hydrogen catalysed by gold/titanium dioxide at temperatures of 40-80°C. Commercially available titanium dioxide (anatase) coated with nanoscale gold particles is used as the catalyst. More drastic reaction conditions, such as e.g. increasing the temperature to >100°C or increasing the pressure, do not lead to an increase in productivity. In addition to the relatively low propene conversions, this process has the great disadvantage that all the catalysts deactivate severely in the course of time. Typical half-lives under normal pressure at 50°C are 30-150 minutes. The increase in temperature and/or pressure described shorten the half-lives further.

Catalysts in which gold particles are applied to a support comprising dispersed titanium centres on an inorganic silicon matrix are also known (WO 98 00415 A1; WO 98 00414 A 1 and EP 0 827 779 A1). All these materials obtained by
5 impregnation with subsequent calcining show relatively low propene conversions, they deactivate in the course of time (typical half-lives are 5-50 h), and therefore cannot be employed in large-scale industrial plants.

10 Catalysts in which gold particles are applied to microporous, crystalline matrix silicates of defined pore structure in which silicon tetrahedral spaces are substituted isomorphically by titanium (e.g. TS-1, TS-2, Ti zeolites, such as Ti-Beta, Ti-ZSM-48, or titanium-
15 containing, mesoporous molecular sieves, such as e.g., Ti-MCM-41 or Ti-HMS) are furthermore known (WO 9800413 A1). Although all these gold-silicalite or gold-zeolite structures show good selectivities, the conversions of the hydrocarbons and above all the catalyst lives are
20 completely inadequate for use in the chemical industry.

The processes described for the catalyst preparation are extremely unsatisfactory in respect of catalyst activity and life. For industrial processes which operate with
25 catalysts of low activity, enormous reactors are required. Short catalyst lives mean a loss of production during the regeneration phase or require a redundant, cost-intensive production route.

30 It is known to employ organic-inorganic hybrid materials based on carbosiloxanes as components of coatings (e.g. EP-A-743 313).

A development of new catalysts which can achieve high activities with excellent selectivities and with lives which are of interest industrially is thus desirable.

- 5 An object of the present invention was thus to provide new catalysts with high activities with simultaneously excellent selectivities.

10 Another object was to develop a process for the preparation of these catalysts.

15 Another object was to provide a technologically simple gas phase process for the selective oxidation of hydrocarbons with a gaseous oxidizing agent on these catalysts, which leads to high yields and low costs at high activities, very high selectivities and catalyst lives which are of interest industrially.

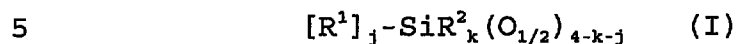
20 Another object was to provide an alternative catalyst for the direct oxidation of hydrocarbons.

Another object was to at least partly eliminate the disadvantages of the known catalysts.

25 These objects are achieved according to the invention by supported compositions comprising particles of gold and/or silver and titanium-containing, organic-inorganic hybrid materials.

30 Organic-inorganic hybrid materials in the context of the invention are organically modified amorphous glasses, which are preferably formed in sol-gel processes via hydrolysis and condensation reactions of usually low molecular weight

compounds and contain bridging organic groups in the network. They contain at least one structural element of the formula (I)



wherein

j is 1, 2 or 3 and

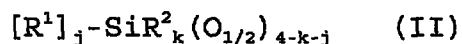
k represents 0, 1 or 2 and

$k + j \leq 3$

10 R^1 is a C_1 - to C_{10} -alkylene radical bridging Si atoms
and

R^2 represents an optionally substituted alkyl or
aryl radical.

15 The organic-inorganic hybrid materials preferably contain a
structural element of the formula (II)



wherein

20 j is 1,

k represents 0, 1 or 2 and

$k + j \leq 3$

R^1 is a C_1 - to C_4 -alkylene radical bridging Si atoms
and

25 R^2 is a methyl or ethyl radical.

The formulation " $O_{1/2}$ " in the formulae (I) and (II)
designates bridging, difunctional oxygen, that is to say
e.g. a structural element Si-O-Si or Si-O-Ti.

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The alkylene radical R^1 in the formulae (I) and (II) is
preferably linked with a chain-like, star-shaped
(branched), cage-like or, particularly preferably, cyclic

structural element. The cyclic structural element can be, for example, $[-O-Si(CH_3)-]_3$ or $[-O-Si(CH_3)-]_4$.

Alkylene radical is understood as meaning all the alkylene, arylene or alkylarylene radicals having in the range from 1 to 10 C atoms known to the expert, such as methylene, ethylene, n-propylene, i-propylene, n-butylene, i-butylene, t-butylene, n-pentylene, i-pentylene, neo-pentylene, n-hexylene, cyclohexylene, i-hexylene, heptylene, octylene, nonylene, decylene and phenylene, it being possible for the radicals to be cyclic or in the form of branched or unbranched chains and to be optionally substituted. Possible substituents are all the radicals which do not react adversely with a catalyst component, such as e.g. titanium or a promoter, such as e.g. alkyl, aryl or alkoxy radicals.

In a particularly preferred embodiment of the invention, the organic-inorganic hybrid materials contain one or more of the following structural elements:

- a) $Si[(C_2H_4)Si(CH_3)_2(O_{1/2})]_4$
- b) $cyclo-\{OSi(CH_3)[(C_2H_4)Si(CH_3)_2(O_{1/2})]\}_4$
- c) $cyclo-\{OSi(CH_3)[(C_2H_4)Si(CH_3)(O_{1/2})_2]\}_4$
- d) $cyclo-\{OSi(CH_3)[(C_2H_4)Si(O_{1/2})_3]\}_4$

The organic-inorganic hybrid materials in the context of the invention comprise between 0.1 and 6 wt.% titanium, preferably between 0.8 and 5 wt.%, particularly preferably between 1.5 and 4 wt.%. The titanium is present in oxidic form and is preferably incorporated or bonded chemically into the organic-inorganic hybrid material via Si-O-Ti bonds.

At higher titanium contents, the catalytic activity of these materials appears to be able to be increased non-linearly with the total titanium content. This has indicated to us that not all the titanium centres have the same catalytic activity. We assume that in active catalysts titanium is bonded to silicon via heterosiloxane bonds.

In addition to titanium, the organic-inorganic hybrid materials according to the invention can comprise further foreign oxides, so-called promoters, from group 5 of the period table according to IUPAC (1985), such as vanadium, niobium and tantalum, particularly preferably tantalum, group 8, particularly preferably Fe, metals of group 15, such as arsenic, antimony and bismuth, particularly preferably antimony, and metals of group 13, such as boron, aluminium, gallium, indium and thallium, particularly preferably aluminium and boron.

These promoters are for the most part present in homogeneous form, i.e. with little formation of domains. The incorporated promoters "M" are present in the organic-inorganic hybrid materials in highly disperse form and are mostly bonded via element-O-Si bonds. The chemical composition of these materials can vary over wide ranges. The proportion of the promoter element is in the range of 0-10%. Several different promoters can of course also be employed. The promoters are preferably employed in the form of promoter precursor compounds which are soluble in the particular solvent, such as promoter salts or organic promoter compounds.

These promoters can increase both the catalytic activity of the composition and the life of the composition during catalytic oxidation reactions of hydrocarbons.

- 5 Organic-inorganic hybrid materials of high specific surface area are preferred. The specific surface area should be at least 1 m²/g, preferably in the range of 25-700 m²/g.

10 Organic-inorganic hybrid materials with a modified surface are furthermore preferred. Modified surface in the context of the invention means that the content of surface silanol groups has been reduced by covalent or coordinate bonding of groups chosen from silicon-alkyl, silicon-aryl, fluorine-containing alkyl and/or fluorine-containing aryl
15 groups.

The supported composition according to the invention comprises gold and/or silver on the organic-inorganic hybrid material as the support material. In the
20 catalytically active state, gold and/or silver are chiefly present as the elemental metal (analysis by X-ray absorption spectroscopy). Small gold and/or silver contents can also be present in a higher oxidation state. Judging by TEM photographs, the largest proportion of the
25 gold and/or silver present is on the surface of the support material. It is in the form of clusters of gold and/or silver on the nanometre scale. The gold particles preferably have a diameter in the range from 0.5 to 50 nm, preferably 0.5 to 15 nm, and particularly preferably 0.5 to
30 10 nm. The silver particles preferably have a diameter in the range from 0.5 to 100 nm, preferably 0.5 to 40 nm, and particularly preferably 0.5 to 20 nm.

The gold concentration should be in the range from 0.001 to 4 wt.%, preferably 0.001 to 2 wt.%, and particularly preferably 0.005-1.5 wt.% of gold.

- 5 The silver concentration should be in the range from 0.005 to 20 wt.%, preferably 0.01 to 15 wt.%, and particularly preferably 0.1 to 10 wt.% of silver.

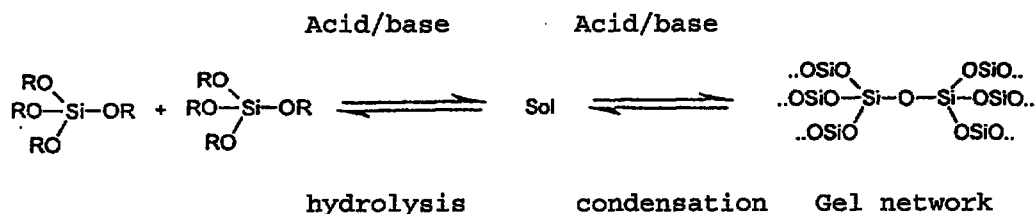
10 Higher gold and/or silver concentrations than the ranges mentioned do not have the effect of increasing the catalytic activity. For economic reasons, the noble metal content should be the minimum amount necessary to achieve the highest catalyst activity.

- 15 The objects described are furthermore achieved by a process for the preparation of the supported compositions comprising particles of gold and/or silver and Ti-containing, organic-inorganic hybrid materials.

- 20 The Ti-containing, organic-inorganic hybrid materials are prepared via sol-gel processes. This preparation is effected, for example, by mixing suitable, usually low molecular weight compounds in a solvent, after which the hydrolysis and/or condensation reactions are initiated by
25 addition of water and optionally catalysts (e.g. acids, bases and/or organometallic compounds). The procedure of such sol-gel processes is known in principle to the expert.

- 30 Suitable low molecular weight compounds are e.g. organic-inorganic binders and precursors of silicon, titanium and promoter. Low molecular weight in the context of the invention means monomeric or oligomeric.

The sol-gel process is based on the polycondensation of hydrolysed, colloiddally dissolved metal component mixtures (sol) to form an amorphous, three-dimensional network (gel). The following equation serves as an illustration of this



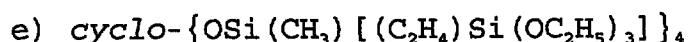
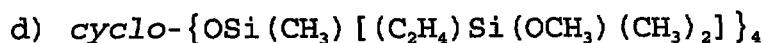
Suitable starting materials are organic-inorganic binders and all the soluble titanium and silicon compounds known to the expert which can be used as a precursor for the corresponding oxides or hydroxides, such as the corresponding alkoxides, soluble salts and organotitanium or -silicon compounds.

Although all salts, such as e.g. halides, nitrates and hydroxides, can be used, the alkoxides, e.g. ethoxide, propoxide etc., of these metals are preferred.

Organic-inorganic binders in the context of the invention are polyfunctional organosilanes, e.g. polyfunctional silanols and/or alkoxides having at least 2 silicon atoms bridged via a C1 to C10-alkylene radical.

Preferred organic-inorganic binders which may be mentioned are:

- a) $\text{Si}[(\text{C}_2\text{H}_4)\text{Si}(\text{OH})(\text{CH}_3)_2]_4$
- b) $\text{cyclo-}\{\text{OSi}(\text{CH}_3)[(\text{C}_2\text{H}_4)\text{Si}(\text{OH})(\text{CH}_3)_2]\}_4$
- c) $\text{cyclo-}\{\text{OSi}(\text{CH}_3)[(\text{C}_2\text{H}_4)\text{Si}(\text{OC}_2\text{H}_5)_2(\text{CH}_3)]\}_4$



5 Syntheses of organic-inorganic binders and processes for carrying out sol-gel processes with these are described, for example, in EP 0743 313, EP 0787 734 and WO 98/52992.

10 Suitable silicon precursors are, for example, silicon alkoxides, such as e.g. $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Si}(\text{OCH}_3)_4$, $(\text{H}_3\text{C})\text{Si}(\text{OC}_2\text{H}_5)_3$ and $(\text{C}_6\text{H}_5)\text{Si}(\text{OC}_2\text{H}_5)_3$. Instead of monomeric alkoxides, condensation products thereof can also be used. $\text{Si}(\text{OC}_2\text{H}_5)_4$ condensates e.g. are commercially obtainable. Polymeric systems, such as e.g. poly(diethoxysiloxane), can furthermore also be employed.

15 Suitable titanium precursor compounds as catalytic titanium species are known from the prior art, such as soluble titanium salts (e.g. titanium halides, nitrates and sulfates), titanium salts of inorganic or organic acids and
20 titanate acid esters.

Titanium derivatives, such as tetraalkyl titanates with alkyl groups of $\text{C}_1\text{-C}_6$, such as methyl, ethyl, n-propyl, n-butyl, iso-butyl, tert-butyl etc., or other organic
25 titanium species, such as titanate acetylacetonate and dicyclopentadienyltitanium dichloride, are preferably used. Tetra-n-butyl orthotitanate, titanium acetylacetonate, titanocene dichloride and titanium tetrachloride are preferred titanium precursor compounds. The titanium
30 precursor compounds can also be employed in the presence of complexing components, such as e.g. acetylacetone or ethyl acetoacetate.

Suitable promoter precursor compounds are, for example, promoter salts, promoter complex compounds, organic promoter compounds or promoter alkoxides. Alkoxide compounds are preferably employed.

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Preferred solvents for the sol-gel process are alcohols, such as e.g. methanol, ethanol, isopropanol or butanol, ketones, such as e.g. acetone, and ethers, such as e.g. THF or tert-butyl methyl ether.

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In principle, any procedure known to the expert for sol-gel processes is possible for synthesis of the Ti-containing, organic-inorganic hybrid materials according to the invention. -Si-O-Ti- groups are generated, for example, by simultaneous hydrolysis and/or condensation of Si precursors and Ti precursors, by reaction of the organic-inorganic binders with Ti precursors, optionally with subsequent addition of the Si precursors, or by simultaneous reaction of organic-inorganic binders, Ti precursors and Si precursors.

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In a preferred embodiment, the Si precursor is initially introduced into a solvent and partly hydrolysed with a deficit of water, based on the amount needed theoretically, and with the addition of a catalyst, the Ti compound is then added, further water is added, optionally with catalyst, and the organic-inorganic binder is then added.

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After the gel formation, which can take place after a few minutes to some days, depending on the composition, the catalyst, the amount of water and the temperature, the gel is dried immediately or after an ageing period of up to 30 days. To bring the hydrolysis and condensation reactions

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to completion, one or more treatments of the moist and/or already dried gel with an excess of water or water vapour can optionally be carried out. Drying is preferably carried out between 50 and 250°C, particularly preferably
5 between 100 and 180°C.

The materials can optionally be comminuted to powders (e.g. by grinding) before or after the drying or employed as shaped bodies.

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The noble metals can be added in the form of precursor compounds, such as salts or organic complexes, or compounds during the sol-gel process, or applied in a known manner, e.g. by impregnation or precipitation, after preparation of
15 the gel. Surface modification of the composition optionally follows this step.

The surface modification can be carried out both before and after the coating with noble metal.

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Modification in the context of the invention is understood as meaning, in particular, application of groups chosen from silicon-alkyl, silicon-aryl, fluorine-containing alkyl or fluorine-containing aryl groups to the surface of the
25 supported composition, the groups being bonded to the functional groups (e.g. OH groups) on the surface by covalent or coordinate bonds. However, any other surface treatment is also expressly included in the scope of the invention.

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The modification is preferably carried out with organosilicon and/or fluorine-containing organosilicon or organic compounds, organosilicon compounds being preferred.

Possible organosilicon compounds are all the silylating agents known to the expert, such as organic silanes, organic silylamines, organic silylamides and derivatives thereof, organic silazanes, organic siloxanes and other organosilicon compounds, which of course can also be employed in combination. Compounds of silicon and partly fluorinated or perfluorinated organic radicals are also expressly subsumed under organosilicon compounds.

Specific examples of organic silanes are chlorotrimethylsilane, dichlorodimethylsilane, chlorobromodimethylsilane, nitrotrimethylsilane, chlorotrimethylsilane, iododimethylbutylsilane, chlorodimethylphenylsilane, chlorodimethylsilane, dimethyl-n-propylchlorosilane, dimethylisopropylchlorosilane, t-butyl dimethylchlorosilane, tripropylchlorosilane, dimethyloctylchlorosilane, tributylchlorosilane, trihexylchlorosilane, dimethylethylchlorosilane, dimethyloctadecylchlorosilane, n-butyl dimethylchlorosilane, bromomethyldimethylchlorosilane, chloromethyldimethylchlorosilane, 3-chloropropyldimethylchlorosilane, dimethoxymethylchlorosilane, methylphenylchlorosilane, triethoxychlorosilane, dimethylphenylchlorosilane, methylphenylvinylchlorosilane, benzyl dimethylchlorosilane, diphenylchlorosilane, diphenylmethylchlorosilane, diphenylvinylchlorosilane, tribenzylchlorosilane and 3-cyanopropyldimethylchlorosilane.

Specific examples of organic silylamines are N-trimethylsilyldiethylamine and pentafluorophenyldimethylsilylamine, and include

N-trimethylsilylimidazoles,
N-t-butyl dimethylsilylimidazole,
N-dimethylethylsilylimidazole, N-dimethyl-n-propyl-
silylimidazole, N-dimethylisopropylsilylimidazole,
5 N-trimethylsilyldimethylamine, N-trimethylsilylpyrrole,
N-trimethylsilylpyrrolidine, N-trimethylsilylpiperidine and
1-cyanoethyl (diethylamino) dimethylsilane.

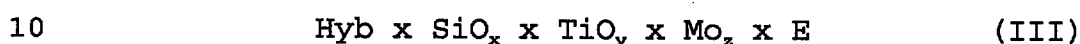
Specific examples of organic silylamides and their
10 derivatives are N,O-bistrimethylsilylacetamide,
N,O-bistrimethylsilyltrifluoroacetamide, N-trimethyl-
silylacetamide, N-methyl-N-trimethylsilylacetamide,
N-methyl-N-trimethylsilyltrifluoroacetamide, N-methyl-N-
trimethylsilylheptafluorobutyramide, N-(t-butyl-
15 dimethylsilyl)-N-tri-fluoroacetamide and
N,O-bis(diethylhydrosilyl) trifluoroacetamide.

Specific examples of organic silazanes are
hexamethyldisilazane, heptamethyldisilazane,
20 1,1,3,3-tetramethyldisilazane, 1,3-bis(chloromethyl)-
tetramethyldisilazane, 1,3-divinyl-1,1,3,3-
tetramethyldisilazane and 1,3-diphenyl-
tetramethyldisilazane.

25 Examples of other organosilicon compounds are N-methoxy-
N,O-bistrimethylsilyltrifluoroacetamide, N-methoxy-N,O-
bistrimethylsilylcarbamate, N,O-bistrimethylsilylsulfamate,
trimethylsilyl trifluoromethanesulfonate and N,N'-
bistrimethylsilylurea.

30 Preferred silylating reagents are hexamethyldisilazane,
hexamethyldisiloxane, N-methyl-N-(trimethylsilyl)-2,2,2-
trifluoroacetamide (MSTFA) and trimethylchlorosilane.

The supported compositions according to the invention comprising particles of gold and/or silver and Ti-containing, organic-inorganic hybrid materials can be described in the dried state, by approximation, by the following empirical formula (the radicals on the surface formed after modification and any incompletely reacted groups are not taken into account here):



Hyb in the formula (III) denotes the constituents formed from the organic-inorganic binder in the sol-gel process, M is a promoter, preferably Ta, Fe, Sb, Al or combinations thereof, x, y and z are the numbers needed effectively to satisfy the valencies of Si, Ti and M and E is the noble metal.

Based on silicon oxide, the content of Hyb in mol per cent can be between 0.05 and 200%. It is preferably between 10 and 120%, particularly preferably between 30 and 100%. The content of titanium oxide based on silicon oxide is between 0.1 and 10 mol%, preferably between 0.5 and 8.0%, particularly preferably between 1.0 and 7.0%. The content of MO_z based on silicon oxide is between 0 and 12 mol%. The content of E based on the noble metal-free composition is between 0.001 and 15 wt.%. In the case of gold, it is preferably between 0.001 and 2 wt.%, and in the case of silver it is preferably between 0.01 and 15 wt.%.

Surprisingly, we have found that the supported compositions according to the invention show a catalytic activity which is higher by several orders of magnitude and good catalyst

lives compared with the catalyst systems known to date for the catalytic oxidation of alkenes and alkanes.

5 The object described is therefore further achieved by the use of the supported compositions according to the invention for the oxidation of hydrocarbons, and the invention also provides this use.

10 The catalysts which have become partly deactivated after a long time can be regenerated again both thermally (up to 250°C) and by washing with suitable solvents, such as e.g. alcohols, or with dilute hydrogen peroxide solutions (e.g. 8% H₂O₂-methanol solution).

15 The composition according to the invention can in principle be applied to all hydrocarbons. The term hydrocarbon is understood as meaning unsaturated or saturated hydrocarbons, such as olefins or alkanes, which can also contain heteroatoms, such as N, O, P, S or halogens. The
20 organic component to be oxidized can be acyclic, monocyclic, bicyclic or polycyclic, and can be monoolefinic, diolefinic or polyolefinic. In the case of organic components with two or more double bonds, the double bonds can be present in conjugated and non-
25 conjugated form. Hydrocarbons which are preferably oxidized are those from which oxidation products are formed which have a partial pressure sufficiently low for constant removal of the product from the catalyst. Unsaturated and saturated hydrocarbons having 2 to 20, preferably 2 to 10
30 carbon atoms, in particular ethene, ethane, propene, propane, isobutane, isobutylene, 1-butene, 2-butene, cis-2-butene, trans-2-butene, 1,3-butadiene, pentene,

pentane, 1-hexene, 1-hexane, hexadienes, cyclohexene, benzene, are preferred.

5 The organic-inorganic hybrid materials allow a type of "catalyst design", i.e. a comprehensive and at the same time controlled influencing of the material properties, such as e.g. the hydrophobicity (polarity) and/or the porosity. Surprisingly, this leads to significantly improved catalysts. The surface polarities have an effect
10 directly on the activities and selectivities of the catalysts. The hydrophobicity of these materials is determined decisively by the number and nature of terminal and above all bridging Si-C bonds. Compared with other organic bonds, such as e.g. Si-O-C bonds, these have the
15 additional advantage that they are to a large degree chemically inert, i.e. are insensitive to hydrolysis and oxidation reactions.

20 In contrast to this, a common feature of all previously known catalysts is the application of gold particles to purely inorganic support materials. Although influencing of the surface polarity is conceivable with these by subsequent modification of the surface, e.g. by application of terminal silicon-alkyl groups, this is only possible to
25 a very limited extent, inter alia depending on the number of reactive groups on the surface (e.g. Si-OH).

The supported compositions can be employed here for oxidation reactions in any desired physical form, e.g.
30 ground powders, spherical particles, pellets, extrudates, granules etc.

A preferred use is the use for the gas phase oxidation of hydrocarbons, in particular olefins, in the presence of oxygen and hydrogen and the supported compositions according to the invention. In this process epoxides are
5 obtained selectively from olefins, ketones are obtained selectively from saturated secondary hydrocarbons and alcohols are obtained selectively from saturated tertiary hydrocarbons. The catalyst lives are some days, months or longer, depending on the educt used.

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The relative molar ratio of hydrocarbon, oxygen, hydrogen and optionally a diluent gas can be varied within wide ranges.

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The molar amount of hydrocarbon employed with respect to the total number of moles of hydrocarbon, oxygen, hydrogen and diluent gas can be varied within wide ranges. An excess of hydrocarbon, based on the oxygen employed (on a molar basis), is preferably employed. The hydrocarbon
20 content is typically greater than 1 mol% and less than 60 mol%. Hydrocarbon contents in the range of 5-35 mol%, particularly preferably 10-30 mol%, are preferably employed. As the hydrocarbon contents increase, productivity is increased and the combustion of hydrogen is
25 reduced.

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The oxygen can be employed in the most diverse forms, e.g. molecular oxygen, air and nitrogen oxide. Molecular oxygen is preferred. The molar oxygen content - with respect to the total number of moles of hydrocarbon, oxygen, hydrogen and diluent gas - can be varied within wide ranges. The oxygen is preferably employed in a molar deficit with respect to the hydrocarbon. Oxygen is preferably employed

in the range of 1-12 mol%, particularly preferably 6-12 mol%. As the oxygen contents increase, the productivity is increased. For safety reasons, an oxygen content of less than 20 mol% should be chosen.

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In the absence of hydrogen, the supported compositions according to the invention show only a very low activity and selectivity. Up to 180°C, the productivity in the absence of hydrogen is low, and at temperatures greater than 200°C large amounts of carbon dioxide are formed, in addition to partial oxidation products. Any known source of hydrogen can be used, such as e.g. molecular hydrogen from the dehydrogenation of hydrocarbons and alcohols. In another embodiment of the invention, the hydrogen can also be generated in situ in a preceding reactor, e.g. by dehydrogenation of propane or isobutane or alcohols, such as e.g. isobutanol. The hydrogen can also be introduced into the reaction system as a species bonded in a complex, e.g. a catalyst-hydrogen complex. The molar hydrogen content - with respect to the total number of moles of hydrocarbon, oxygen, hydrogen and diluent gas - can be varied within wide ranges. Typical hydrogen contents are greater than 0.1 mol%, preferably 5-80 mol%, particularly preferably 10-65 mol%. As the hydrogen contents increase, the productivity is increased.

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A diluent gas, such as nitrogen, helium, argon, methane, carbon dioxide or similar gases which are inert, can optionally also be employed in addition to the essentially necessary educt gases described above. Mixtures of the inert components described can also be employed. The inert component additive is favourable for transportation of the heat liberated from this exothermic oxidation reaction and

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from safety aspects. If the process according to the invention is carried out in the gas phase, gaseous diluent components, such as e.g. nitrogen, helium, argon, methane and possibly water vapour and carbon dioxide, are preferably used. Although water vapour and carbon dioxide are not completely inert, they have a positive effect at very low concentrations (< 2 vol.%).

If the invention is carried out in the liquid phase, an oxidation-stable and thermally stable inert liquid is expediently chosen (e.g. alcohols, polyalcohols, polyethers and halogenated hydrocarbons). The supported compositions according to the invention are also suitable for the oxidation of hydrocarbons in the liquid phase. Both in the presence of organic hydroperoxides (R-OOH), olefins are converted into epoxides in the liquid phase highly selectively on the catalysts described, and in the presence of oxygen and hydrogen olefins are converted into epoxides in the liquid phase highly selectively on the catalysts described.

We have found that the selective oxidation reaction described above has a high sensitivity to the catalyst structure. When nanodisperse particles of gold and/or silver were present in the supported composition, an increase in the productivity to give the selective oxidation product was observed.

The spatially close interaction of gold and/or silver and titanium oxide (perimetric interface) on the organic-inorganic support operates particularly efficiently, i.e. excellent epoxidation catalysts in the presence of oxygen and hydrogen are obtained. The activity of the catalysts

and the catalyst life can optionally be increased further by incorporation of small amounts of promoters, e.g.

foreign metals, above all by incorporation of tantalum and/or iron and/or antimony and/or aluminium. The

5 compositions according to the invention can be prepared on an industrial scale without process technology problems and inexpensively.

10 The characteristic properties of the present invention are illustrated in the following examples with the aid of catalyst preparations and a catalytic test reaction.

It goes without saying that the invention is not limited to the following examples.

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Examples

Instructions for testing the catalysts (test instructions)

- 5 A metal tube reactor of 10 mm internal diameter and 20 cm length which was temperature-controlled by means of an oil thermostat was employed. The reactor was supplied with educt gases with a set of four mass flow regulators (hydrocarbon, oxygen, hydrogen, nitrogen). For the
- 10 reaction, 0.5 g pulverulent catalyst was initially introduced at 150°C under an increased pressure of 1 bar. The educt gases were metered into the reactor from the top. The standard catalyst loading was 4 l/g cat./h. Propene was chosen by way of example as the "standard hydrocarbon".
- 15 For carrying out the oxidation reactions, a gas stream enriched with nitrogen, always called the standard gas composition below, was chosen: $N_2/H_2/O_2/C_3H_6$: 15/65/10/10%. The reaction gases were analysed quantitatively by gas chromatography. The individual reaction products were
- 20 separated by gas chromatography by a combined FID/TCD method in which the products flow through three capillary columns:
- FID: HP-Innowax, 0.32 mm internal diameter, 60 m long, 0.25 μ coating thickness.
- 25 TDC: HP-Plot Q, 0.32 mm internal diameter, 30 m long, 20 μ coating thickness
HP-Plot Molsieve 5 A, 0.32 mm internal diameter, 30 m long, 12 μ coating thickness
connected in series.

Example 1:

This example describes the preparation of a catalyst comprising a titanium-containing, organic-inorganic hybrid material which was modified on the surface and subsequently coated with gold particles. The binder content is 40% and the titanium oxide content is 4.5%.

3.5 g of a 0.1 N solution of p-toluenesulfonic acid in water were added to 40.7 g tetraethoxysilane (195.4 mmol) and 21.1 g ethanol (analytical grade) and the mixture was stirred for 1 hour. 4.0 g tetrabutoxytitanium (11.75 mmol) were then slowly added, the mixture was stirred for a further 30 minutes, a solution of 8.44 g cyclo- $\{OSi(CH_3)[(C_2H_4)Si(OH)(CH_3)_2]\}_4$ (13 mmol) in 20.0 g ethanol (analytical grade) was added, the mixture was stirred again for 30 minutes, a mixture of 3.9 g of a 0.1 N solution of p-toluenesulfonic acid in water and 3.9 g ethanol (analytical grade) was added, while stirring, and the mixture was finally left to stand. After approx. 24 h the mixture reaches the gel point. After an ageing time of approx. 14 days, water was added to the gel until no further formation of gas bubbles and streaks was detectable. The water is exchanged several times here. The product was then heated at 60°C in water for a further hour, the supernatant solution was decanted off and the residue was dried at 150°C for 8 hours.

The resulting catalyst support has a theoretical composition of 40% cyclo- $\{OSi(CH_3)[(C_2H_4)Si(CH_3)_2(O_{1/2})]\}_4$, 55.6% SiO₂ and 4.5% TiO₂.

For modification of the surface, 20 g powder were initially introduced into the reaction vessel with 20 g 1,1,1,3,3,3-hexamethyldisilazane in 200 g dry n-hexane under an inert gas and the mixture was heated under reflux for 2 hours, while stirring. The supernatant solution was then decanted off and the residue was washed twice with 300 ml n-hexane each time, freed from volatile constituents in vacuo and dried at 150°C for 4 hours.

10 The BET surface area is 345 m²/g.

2.5 g of titanium-containing support were initially introduced into 20 ml methanol (Merck, analytical grade), 40 mg HAuCl₄ x 3 H₂O (0.1 mmol, Merck), dissolved in 5 ml methanol, were added, the pH was brought to 8 with 0.8 ml 2 N K₂CO₃, the mixture was stirred for 30 min, 2 ml sodium citrate solution were added, the pH was checked again, the mixture was stirred for 120 min and the solid was separated off, washed 3 x with 20 ml methanol each time, dried at 120°C under normal pressure for 10 h and calcined at 200°C for 5 h. The gold content of the gold-titanium-silicon catalyst is 0.58 wt.% (ICP analysis).

In a test according to the test instructions, propene conversions of 1.5% were achieved over 50 h at constant PO selectivities of 95%.

Example 2:

30 This example describes the preparation of a catalyst analogously to example 1 comprising a titanium-containing, organic-inorganic hybrid material which was modified on the surface and subsequently coated with gold particles. The

catalyst support was ground before being coated with noble metal.

5 For the grinding, the titanium-containing material was suspended in isopropanol and ground in a ball mill, the solvent was removed on a rotary evaporator and the powder was dried at 150°C under normal pressure for 4 hours, subsequently modified on the surface and coated with noble metal.

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In a test according to the test instructions (140°C), propene conversions of 2.5% were achieved over 50 h at constant PO selectivities of 95%. In a test according to the test instructions at 150°C, propene conversions of 3.4%
15 were achieved over 50 h at constant PO selectivities of 95%.

Example 3:

20 This example describes the preparation of a catalyst comprising a titanium-containing, organic-inorganic hybrid material which was modified on the surface and subsequently coated with gold particles. The preparation was carried out analogously to example 2, but the binder content is 20%
25 and the titanium dioxide content is 3%.

4.8 g of a 0.1 N solution of p-toluenesulfonic acid in water are added to 55.6 g tetraethoxysilane (266.9 mmol) and 16.9 g ethanol (analytical grade) and the mixture is
30 stirred for 1 hour. 2.65 g tetrabutoxytitanium (7.78 mmol) are then slowly added, the mixture is stirred for a further 30 minutes, a solution of 4.16 g cyclo-
 $\{\text{OSi}(\text{CH}_3)[(\text{C}_2\text{H}_4)\text{Si}(\text{OH})(\text{CH}_3)_2]\}_4$ (6.4 mmol) in 10.0 g ethanol

(analytical grade) is added, the mixture is stirred again for 30 minutes, a mixture of 5.1 g of a 0.1 N solution of p-toluenesulfonic acid in water and 5.1 g ethanol (analytical grade) is added, while stirring, and the
5 mixture is finally left to stand. After approx. 24 h the mixture reaches the gel point. After an ageing time of approx. 18 days water is added to the gel until no further formation of gas bubbles and streaks is detectable. The water is exchanged several times here. The product is then
10 heated at 60°C in water for a further hour, the supernatant solution is decanted off and the residue is dried at 150°C for 8 hours. A yield of 21.9 g is obtained. The BET surface area is 118 m²/g.

15 The catalyst support obtained has a theoretical composition of 20% $\text{cyclo-}\{\text{OSi}(\text{CH}_3)[(\text{C}_2\text{H}_4)\text{Si}(\text{CH}_3)_2(\text{O}_{1/2})]\}_4$, 77% SiO_2 and 3% TiO_2 .

The resulting catalyst support is then modified on the
20 surface. For this, 10 g of product are initially introduced into the reaction vessel with 10 g 1,1,1,3,3,3-hexamethyldisilazane in 100 g dry n-hexane under an inert gas and the mixture is heated under reflux for 2 hours. The supernatant solution is then decanted off and the
25 residue is washed twice with 150 ml n-hexane each time, freed from volatile constituents in vacuo and dried at 150°C for 4 hours.

2.5 g of titanium-containing support were initially
30 introduced into 20 ml methanol (Merck, analytical grade), 40 mg $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ (0.1 mmol, Merck), dissolved in 5 ml methanol, were added, the pH was brought to 8 with 0.8 ml 2 N K_2CO_3 , the mixture was stirred for 30 min, 2 ml sodium

citrate solution were added, the pH was checked again, the mixture was stirred for 120 min and the solid was separated off, washed 3 x with 20 ml methanol each time, dried at 120°C under normal pressure for 10 h and calcined at 200°C for 5 h. The gold content of the gold-titanium-silicon catalyst is 0.55 wt.% (ICP analysis).

In a test according to the test instructions, propene conversions of 0.5% were achieved over 50 h at constant PO selectivities of 95%.

Example 4:

This example describes the preparation of a catalyst comprising a titanium-containing, organic-inorganic hybrid material which was modified on the surface and subsequently coated with gold particles. The preparation was carried out analogously to example 2, but the titanium oxide content is 3%.

10.8 g of a 0.1 N solution of p-toluenesulfonic acid in water are added to 123.3 g tetraethoxysilane (591.8 mmol) and 62.1 g ethanol (analytical grade) and the mixture is stirred for 1 hour. 7.95 g tetrabutoxytitanium (23.3 mmol) are then slowly added, the mixture is stirred for a further 30 minutes, a solution of 24.93 g cyclo- $\{\text{OSi}(\text{CH}_3)[(\text{C}_2\text{H}_4)\text{Si}(\text{OH})(\text{CH}_3)_2]\}_4$ (38.5 mmol) in 60.0 g ethanol (analytical grade) is added, the mixture is stirred again for 30 minutes, a mixture of 11.4 g of a 0.1 N solution of p-toluenesulfonic acid in water and 11.4 g ethanol (analytical grade) is added, while stirring, and finally the mixture is left to stand. After approx. 24 h the mixture reaches the gel point. After an ageing time of

approx. 10 days water is added to the gel until no further formation of gas bubbles and streaks is detectable. The water is exchanged several times here. The product is then heated at 60°C in water for a further hour, the supernatant solution is decanted off and the residue is dried at 150°C for 8 hours. A yield of 63.4 g is obtained.

The catalyst support obtained has a theoretical composition of 40% $\text{cyclo-}\{\text{OSi}(\text{CH}_3)[(\text{C}_2\text{H}_4)\text{Si}(\text{CH}_3)_2(\text{O}_{1/2})]\}_4$, 57% SiO_2 and 3% TiO_2 .

The catalyst support is then modified on the surface. For this, 25 g of product are initially introduced into the reaction vessel with 25 g 1,1,1,3,3,3-hexamethyldisilazane in 250 g dry n-hexane under an inert gas and the mixture is heated under reflux for 2 hours. The supernatant solution is then decanted off and the residue is washed twice with 400 ml n-hexane each time, freed from volatile constituents in vacuo and dried at 150°C for 4 hours. The BET surface area is 264 m²/g.

2.5 g of titanium-containing support were initially introduced into 20 ml methanol (Merck, analytical grade), 40 mg $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ (0.1 mmol, Merck), dissolved in 5 ml methanol, were added, the pH was brought to 8 with 0.8 ml 2 N K_2CO_3 , the mixture was stirred for 30 min, 2 ml sodium citrate solution were added, the pH was checked again, the mixture was stirred for 120 min and the solid was separated off, washed 3 x with 20 ml methanol each time, dried at 120°C under normal pressure for 10 h and calcined at 200°C for 5 h. The gold content of the gold-titanium-silicon catalyst is 0.58 wt.% (ICP analysis).

In a test according to the test instructions, propene conversions of 1.5% were achieved over 50 h at constant PO selectivities of 95%.

5 **Example 5:**

10 This example describes the preparation of an amorphous catalyst support comprising an organic-inorganic hybrid material and the oxides of silicon, titanium and tantalum, which was modified on the surface and subsequently coated with gold particles.

15 The catalyst preparation is carried out analogously to example 2, but 60 min after the addition of tetrabutoxytitanium, 2.4 g Ta(OEt)₅ (6 mmol, Chempur, 99.9%) are added to the homogeneous mixture, the mixture is stirred for 15 min and, analogously to example 2, a carbosilane crosslinking agent is added, the mixture is gelled and worked up and the product is modified and coated with gold.

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In a test according to the test instructions, propene conversions of 2.7% were achieved over 50 h at constant PO selectivities of 94%.

25

Example 6

30 This example describes the preparation of a catalyst comprising a titanium-containing, organic-inorganic hybrid material which is modified on the surface and subsequently coated with silver particles. The catalyst preparation was carried out analogously to example 2. The catalyst support

is coated with silver particles instead of with gold particles.

2.5 g of titanium-containing catalyst support were added to
5 a solution of 150 mg silver nitrate (0.97 mmol; Merck) in
25 ml methanol at room temperature, while stirring. The
suspension was stirred at RT for 1 h and the solid was
separated off and washed once with 20 ml methanol. The
moist, white solid was dried at 120°C for 3 h and then
10 calcined in air at 150°C for 2 h and at 200°C for 5 h.

In a test according to the test instructions, stationary
propene conversions of 0.3% were achieved over 50 h at
constant PO selectivities of 94%.

15

Example 7

Trans-2-Butene is employed instead of propene as the
unsaturated hydrocarbon. A catalyst comprising an organic-
20 inorganic hybrid material and the oxides of silicon and
titanium and metallic gold is used for the partial
oxidation of trans-2-butene. The catalyst preparation is
carried out analogously to example 2.

25 In a test according to the test instructions, trans-2-
butene conversions of 2.0% were achieved over 50 h at
constant 2,3-epoxybutane selectivities of 91%.

Example 8

30

Cyclohexene is chosen instead of propene as the unsaturated
hydrocarbon. A catalyst comprising an organic-inorganic
hybrid material and the oxides of silicon, titanium and

metallic gold is used for the partial oxidation of cyclohexene. The catalyst preparation is carried out analogously to example 2. Cyclohexene is brought into the gas phase with the aid of an evaporator.

5

In a test according to the test instructions, cyclohexene conversions of 1.8% were achieved over 50 h at cyclohexene oxide selectivities of 90%.

10 **Example 9**

1,3-Butadiene is chosen instead of propene as the unsaturated hydrocarbon. A catalyst comprising an organic-inorganic hybrid material and the oxides of silicon,
15 titanium and metallic gold is used for the partial oxidation of 1,3-butadiene. The catalyst preparation is carried out analogously to example 2.

In a test according to the test instructions, butadiene
20 conversions of 0.6% were achieved over 40 h at butene oxide selectivities of 85%.

Example 10

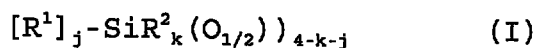
25 Propane is employed instead of propene, as a saturated hydrocarbon. A catalyst comprising an organic-inorganic hybrid material and the oxides of silicon, titanium and metallic gold is used for the partial oxidation of propane. The catalyst preparation is carried out analogously to
30 example 2.

In a test according to the test instructions, propane conversions of 0.4% were achieved over 40 h at acetone selectivities of 80%.

Patent claims

1. Supported compositions, characterized in that they
comprise particles of gold and/or silver and titanium-
5 containing, organic-inorganic hybrid materials.

2. Supported compositions according to claim 1,
characterized in that the organic-inorganic hybrid
materials contain at least one structural element of
10 the formula (I)



wherein

j is 1, 2 or 3 and

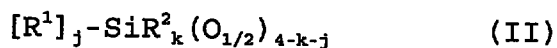
15 k represents 0, 1 or 2 and

$k + j \leq 3$

R^1 is a C_1 - to C_{10} -alkylene radical bridging Si
atoms and

R^2 represents an optionally substituted alkyl
20 or aryl radical.

3. Supported compositions according to one or more of
claims 1 to 2, characterized in that the organic-
inorganic hybrid materials contain at least one
25 structural element of the formula (II)



wherein

j is 1,

30 k represents 0, 1 or 2 and

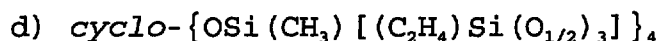
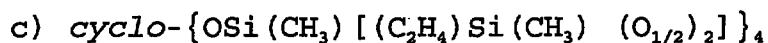
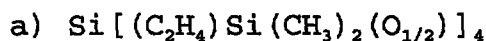
$k + j \leq 3$

R^1 is a C_1 - to C_4 -alkylene radical bridging Si
atoms and



R^2 is a methyl or ethyl radical.

4. Supported compositions according to one or more of claims 1 to 3, characterized in that the organic-inorganic hybrid materials contain at least one of the following structural elements



5. Supported compositions according to one or more of claims 1 to 4, characterized in that the organic-inorganic hybrid materials comprise between 0.1 and 6 wt.% titanium and optionally further foreign oxides, so-called promoters.

6. Supported compositions according to one or more of claims 1 to 5, characterized in that they comprise between 0.001 and 4 wt.% gold or between 0.01 and 8 wt.% silver or a mixture of gold and silver.

7. Supported compositions according to one or more of claims 1 to 6, characterized in that the surface thereof has been modified.

8. Process for the preparation of the supported compositions according to claims 1 to 7, characterized in that the titanium-containing, organic-inorganic hybrid materials are prepared via sol-gel processes.



9. Process according to claim 8, characterized in that organic-inorganic binders and silicon precursors, titanium precursors and optionally promoter precursors are mixed.

5

10. Process according to claim 9, characterized in that the organic-inorganic binders are polyfunctional organosilanes having at least 2 silicon atoms bridged via a C1 to C10-alkylene radical.

10

11. Process according to one or more of claims 8 to 10, characterized in that the organic-inorganic hybrid materials are modified on the surface and/or coated with particles of gold and/or silver, the noble metal being present on the nanometre scale.

15

12. Use of the composition according to one or more of claims 1 to 7 as a catalyst for the selective oxidation of hydrocarbons.

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13. Use according to claim 12, characterized in that propene is oxidized to propene oxide.

14. Process for the selective oxidation of hydrocarbons in the presence of one or more supported compositions according to one or more of claims 1 to 7 and of molecular oxygen and hydrogen.

25