

Metallic reaction tube having a catalytic coating

The present invention relates to a metallic reaction tube having a catalytic coating, preferably on the inner wall of the tube, tube-bundle reactors comprising coated reaction tubes, a coating process and a use of the reaction tube or of the tube-bundle reactor in the catalytic gas-phase oxidation for the preparation of (meth)acrolein and/or (meth)acrylic acid.

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A large number of chemical reactions are carried out under heterogeneous catalysis in reaction tubes. The catalysts are as a rule used in the form of unsupported or supported catalysts and are introduced in the form of a bed into the reaction tubes. However, filled reaction tubes are disadvantageous, in particular with regard to the large pressure drop and the high weight of the filled tube itself. This generally necessitates a greater wall thickness, with adverse effects on the heat transfer. These disadvantages are overcome by applying a catalytic coating to the inner walls of the tube.

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WO 97/25146 discloses a catalytic coating which consists of a composite comprising a metallic substrate, for example the inside of a reaction tube, an adhesion promoter and a catalytic top layer of, in particular, oxide ceramic catalyst material. To avoid flaking of the catalytic top layer under changing thermal stress, it is then essential first to apply an adhesion promoter having an essentially metallic composition to the metallic substrate.

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German Laid-Open Application DOS 21 18 871 discloses that the formation of byproducts in the preparation of carboxylic acids or their anhydrides by gas-phase catalytic oxidation of aromatic or unsaturated aliphatic hydrocarbons in the presence of vanadium pentoxide-containing supported catalysts in a tube-

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bundle reactor can be reduced by coating the inner wall of the tubes at least partly with a catalytic material which contains titanium dioxide, preferably mixed with vanadium pentoxide. The products of the process are
5 obtained in high purity and high yields. The description contains no information on a reduction of the hot spot temperatures in the tubes.

An industrially important reaction under heterogeneous
10 catalysis is the catalytic gas-phase oxidation of C_1 - C_6 -alkanes, C_2 - C_6 -alkenes, C_1 - C_6 -alkanols and/or C_1 - C_6 -alkanals and/or precursors thereof for the preparation of (meth)acrolein and/or (meth)acrylic acid. These reactions are highly exothermic and, owing to a large
15 number of possible simultaneous or subsequent reactions, it is therefore necessary to control the reaction temperature in order to achieve a selective reaction. For temperature regulation, the reaction tubes are surrounded by a heat transfer medium, for
20 example by a salt melt. In spite of this thermostating, hot spots, which have a higher temperature than the rest of the catalyst bed, form along the catalyst bed. This reduces the catalyst life in this catalyst tube section on the one hand and, on
25 the other hand, adversely affects the selectivity of the acrolein/acrylic acid formation.

Various countermeasures for overcoming said disadvantage have already been recommended in the prior
30 art and are described, for example, in DE-A-44 31 949. One proposal involves reducing the diameter of the catalyst tubes in order in this way to increase the removal of heat per unit volume of the catalyst. The disadvantage of this method, however, is that it
35 inevitably increases the number of catalyst-filled catalyst tubes required for a specific production rate, which increases both the production costs of the reactor and the time required for filling and emptying the catalyst tubes in the catalyst.

According to another proposed process, an attempt is made to suppress the formation of the hot spots by varying the volume-specific activity of the catalytic load along the catalyst tubes. However, this procedure requires either the use of at least two catalysts of different activities or the presence of inert material. Moreover, this procedure complicates the filling of the catalyst tubes. Another obvious possibility for reducing hot spot formation consists in reducing the acrolein loading of the reactor. However, this measure simultaneously reduces the space-time yield of desired product.

DE-A-44 31 949 discloses a reduction of the hot spot temperatures in the tubes of a tubular reactor with circulation of heat-exchange medium in the space surrounding the catalyst tubes by passing the heat-exchange medium along a meandering path cocurrently with the reaction gases and by maintaining specific, small temperature differences of the heat-exchange medium from the point of entry to the point of exit from the reactor.

It is an object of the present invention to provide a reaction tube or a tube-bundle reactor comprising reaction tubes, which are designed in such a way that, when gas-phase oxidations under heterogeneous catalysis are carried out in such reaction tubes, the occurrence of hot spots is predominantly or completely avoided. This object is to be achieved in a simple manner by a suitable formation of the reaction tubes, without the temperature profile and flow of the circulation of heat-exchange medium having to meet particular requirements.

We have found that this object is achieved, according to the invention, by providing a metallic reaction tube having a catalytic coating, wherein the coating contains a multimetal oxide material which is applied

directly to the reaction tube.

We have found, surprisingly, that a coating which contains a multimetal oxide material and is applied directly to a metallic reaction tube without an
5 adhesion-promoting intermediate layer constitutes a composite which is stable over a long time and to temperatures of up to about 600°C, as usually occur in catalytic gas-phase oxidation.

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It is also intended to provide a coating process for the production of the corresponding metallic reaction tubes or tube-bundle reactors.

15 The term "multimetal oxide material" used here refers to oxide mixtures which contain two or more, preferably three or more, chemical elements, in general not more than 50 different chemical elements being present in an amount of more than 1% by weight. The transition metal
20 elements molybdenum and bismuth are always present in the multimetal oxide materials used according to the invention. Usually, the multimetal oxide materials are not simple physical mixtures of oxides of the elemental constituents but heterogeneous mixtures of complex
25 polycompounds of these elements.

The multimetal oxide materials used according to the invention contain, as a rule, molybdenum in an amount from 20 to 90, preferably from 30 to 80, particularly
30 preferably from 40 to 70, % by weight, calculated as MoO_3 .

The catalytic coating containing the multimetal oxide material is applied directly to the reaction tube, i.e.
35 without auxiliary supports arranged in between or adhesion-promoting intermediate layers.

Preferably, the inner wall of the metallic reaction tube is provided with the catalytic coating.

There are in principle no restrictions regarding the metallic materials for the reaction tube, but steel, in particular stainless steel, such as V₂A stainless steel, and ferritic steel, are preferred.

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The catalytic coating according to the invention preferably has a coat thickness of from 10 to 1000 μm , preferably from 20 to 500 μm , particularly preferably from 50 to 350 μm .

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In a preferred embodiment, the present invention relates to tube-bundle reactors comprising metallic reaction tubes which are provided, in accordance with the above statements, with a catalytic coating which

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contains a multimetal oxide material applied directly to the reaction tubes, preferably to the inner wall of the tubes. The reaction tubes of the tube-bundle

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reactor may have any desired cross-section, which, however, is generally round, in particular circular. The internal diameter of the tubes is preferably from 0.2 to 70 mm, in particular from 10 to 50 mm, particularly preferably from 15 to 30 mm. The tube-bundle reactor can, as a rule, contain up to 50,000, preferably from 50 to 40,000, particularly preferably

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from 500 to 30,000, reaction tubes. The tube length is, as a rule, from 0.1 to 10 m, preferably from 0.3 to 8 m, particularly preferably from 0.5 to 6 m.

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According to a particular embodiment, it is possible to introduce into the reaction tubes, preferably in their totality, a bed of unsupported or coated catalysts comprising multimetal oxide, in particular to a height of 5 to 90%, preferably from 10 to 70%, especially from 20 to 50%, of the total length of the reactor tube.

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The catalyst bed is preferably installed in the region on the gas exit side.

According to a further preferred embodiment, a second reactor, in particular a tube-bundle reactor, which is

provided with a bed of unsupported or coated catalysts comprising multimetal oxide is connected downstream of a tube-bundle reactor comprising wholly or partly coated reaction tubes. This arrangement of two
5 reactors connected in series has the advantage that, depending on the progress of the reaction, it is possible to work under different, specially adapted process conditions. In particular, it is possible as a rule to employ temperatures about 20 to 100°C higher,
10 typically temperatures of from 200 to 450°C, in the first reactor, whose tubes carry the novel catalytic coating, compared with the conventional gas-phase oxidation to (meth)acrolein and/or (meth)acrylic acid, because of the avoidance of the danger of hot spots.
15 Consequently, owing to improved desorption, there is less loss of starting materials due to total combustion.

The novel coating process comprises the following
20 steps:

- (1) Preparation of solutions, emulsions and/or dispersions of elements and/or compounds of the elements present in the multimetal oxide catalyst and/or multimetal oxide catalyst precursor,
- 25 (2) if required, introduction of adhesion promoters, binders, viscosity regulators and/or pH regulators into the solutions, emulsions and/or dispersions,
- (3) application of the solutions, emulsions and/or dispersions to the reaction tube or the reaction
30 tubes of the tube-bundle reactor, preferably to their inner surface, preferably by spraying or immersion, and
- (4) heating of the coated reaction tube, in the presence or absence of inert or reactive gases, to
35 a temperature of from 20 to 1500°C, preferably from 200 to 400°C, for drying and, if required, sintering or calcining the multimetal oxide catalysts and/or multimetal oxide catalyst precursors.

First, the preparation of a liquid starting mixture in the form of a solution, emulsion and/or dispersion is carried out according to the manner described in DE-A 198 05 719. The liquid mixtures generally contain a liquid chemical component, which is used as solvent, emulsifier or dispersant for the further components of the mixture. Water and/or one or more organic compounds whose boiling point or sublimation temperature at atmospheric pressure is $> 100^{\circ}\text{C}$, preferably $> 150^{\circ}\text{C}$, are preferably used for this purpose. Preferably, the organic fraction of the liquid chemical components to be used according to the invention is from 10 to 80, in particular from 10 to 70, particularly preferably from 20 to 50, % by weight.

In addition to the chemical elements of the solvent or dispersant, the liquid mixtures contain one or more, preferably 2 or more, especially 3 or more, chemical elements, but in general not more than 50 different chemical elements in an amount of more than 1% by weight in each case. The chemical elements are preferably very thoroughly mixed in the mixtures and are present, for example, in the form of a mixture of different miscible solutions, intimate emulsions having a small droplet size and/or preferably as a suspension (dispersion) which contains the relevant chemical elements in general in the form of a finely divided precipitate, for example in the form of a chemical coprecipitate. The use of sols and gels, in particular of those which contain the relevant chemical elements in a substantially homogeneous distribution and preferably those which exhibit adhesion and flow behavior advantageous for the subsequent coating, has also proven particularly useful. Suitable starting compounds for the selected chemical elements are in principle the elements themselves, preferably in finely divided form, and moreover all compounds which contain the selected chemical elements in a suitable form, such as oxides, hydroxides, hydrated oxides, inorganic

salts, preferably nitrates, carbonates, acetates and oxalates, organometallic compounds, alkoxides, etc. The respective starting compounds may be used in solid form or in the form of solutions, emulsions and/or suspensions.

In addition, the liquid mixture may contain further compounds which influence the adhesion properties and the flow behavior of the liquid mixture on the surface to be coated. Organic compounds which may be mentioned here are, for example, ethylene glycol or glycerol, as described in DE-A 44 42 346, or, for example, maleic acid copolymers and, as inorganic compounds, for example, SiO_2 , organosilicon compounds or siloxanes.

Furthermore, the mixtures used may additionally contain an inorganic and/or organic binder or a binder system which stabilizes the mixture used. For example, binders and binder systems which contain metal salts, metal oxides, hydrated metal oxides, phosphates of hydrated metal oxides and/or eutectic compounds melting at the temperature of use of the catalyst are suitable for this purpose.

The mixture may furthermore be brought within a defined pH range by adding acids and/or bases. In many cases, pH-neutral suspensions are used. For this purpose, the mixture can advantageously be brought to a pH from 5 to 9, preferably from 6 to 8. Special results are to be achieved with the novel process if the mixture has a high solids content of up to 95, preferably from 50 to 80, % by weight in combination with a low viscosity.

In a preferred embodiment of the invention, the mixture is stirred after and, in general, also during the preparation, and its flowability is measured continuously, but at least at the end of the preparation. This can be effected, for example, by measuring the current consumption of the stirrer. With

the aid of this measurement, the viscosity of the suspension can be adjusted, for example by adding further solvents or thickeners, so that an optimum adhesion, layer thickness and uniformity of the layer thickness result on the surface to be coated.

In a further process step, the coating with the prepared mixtures is carried out preferably by means of a spray method or by immersion, on various parts of a metallic reaction tube or the tubes of a tube-bundle reactor, in particular on the inner walls of the tubes, to give a layer from 10 to 1000 μm , preferably from 20 to 500 μm , particularly preferably from 50 to 350 μm , thick.

Furthermore, the mixture can be poured into the individual tubes and centrifuged at speeds of from 200 to 1000, preferably from 300 to 800, rpm. In a preferred embodiment, the coating on the inner surface of the reaction tubes are produced by spraying on the abovementioned liquid mixture. The mixture material sprayed on is thus pressed into the rough surface of the substrate, air bubbles under the coating being prevented. The mixture used may adhere completely to the sprayed inner surface. However, some of the mixture may also be discharged again by dripping off, particularly in the case of poor adhesion and/or low viscosity of the mixture. The auxiliary supports to be coated, for example in the form of inner tubes, can be coated wholly or only partly. In particular, the respective reactor tube entrance and reactor tube exit can be excluded from the coating by means of a suitable apparatus, in order to prevent subsequent sealing problems with the apparatuses to be connected for feeding in and removing the fluid. Coating in which the mixture is sprayed into the preheated tube or this mixture is introduced into the preheated tube by immersion has also proven useful. For this purpose, the metallic substrate is preheated to 60 to 500°C,

preferably 200 to 400°C, particularly preferably 200 to 300°C, before the suspension is sprayed on, and is coated at this temperature with the mixture described at the outset. A major part of the volatile components of the mixture evaporate and a preferably from 10 to 2000 μm , especially from 20 to 500 μm , particularly preferably from 50 to 350 μm , thick layer of the catalytically active metal oxides is formed on the metallic substrate. This method of preparation can be effected as described in DE-A-25 10 994, with the modification that the mixture is applied not to a preheated support but to a preheated metallic substrate.

To obtain particularly thick layers or particularly homogeneous coatings, the coating of the reaction tubes can also be carried out several times in succession. The individual coating operations on a reaction tube can be interspersed with separate drying and/or calcination and/or sintering steps. In the case of spraying, the coating of the inner wall is advantageously carried out with the aid of one or more spray lances, preferably with one or more movable spray lances. The spray lance is drawn through the tube to be coated, during the spray process, for example with the aid of an automatic apparatus at a defined constant or varying speed.

The thickness of the applied layer after drying and any calcination or sintering is preferably from 10 to 1000 μm , particularly preferably from 20 to 500 μm .

In addition, the adhesion of the catalytic layer can be increased by a chemical, physical or mechanical pretreatment of the inner tube prior to coating. In the case of a chemical pretreatment, the inner tubes can be pickled, for example with alkalis or preferably with acids. Furthermore, for example, the inner tube can be roughened by blasting with a dry blasting

medium, in particular corundum or quartz sand, in order to assist the adhesion. Moreover, cleaning agents which comprise a suspension of hard particles, e.g. corundum, in a dispersing liquid have also proven
5 useful.

On heating the coated tube-bundle reactor under reduced pressure or under a defined gas atmosphere to temperatures of from 20 to 1500°C, preferably from 60
10 to 1000°C, particularly preferably from 200 to 600°C, very particularly preferably from 250 to 500°C, the coating applied beforehand is freed from the preferably aqueous solvent by drying. At elevated temperatures, sintering or calcination of the particles forming the
15 coating may also take place. In this process, the actual catalytically active coating is generally obtained.

An embodiment of the invention relates to a process for
20 the preparation of (meth)acrolein and (meth)acrylic acid by catalytic gas-phase oxidation of C₁-C₆-alkanes, C₂-C₆-alkenes, C₁-C₆-alkanols and/or C₁-C₆-alkanals and/or precursors using a metallic reaction tube described above and having a catalytic coating or using
25 a tube-bundle reactor described above and comprising reaction tubes having a catalytic coating. Since, in this process, the danger of formation of hot spots is avoided, it is possible to employ a higher temperature, in particular from about 20 to 100°C higher than in the
30 conventional catalytic gas-phase oxidation, typically temperatures of from about 200 to 250°C. The higher temperature results in improved desorption of starting materials with less total combustion.

35 The invention is explained in more detail below with reference to embodiments.

A reaction tube having an internal diameter of 21 mm and a length of 90 cm was fed in each case with

300 l (S.T.P.)/h of a gas mixture having the composition:

3% by volume of propene,

9.5% by volume of oxygen and

5 nitrogen as the remainder.

A multimetal oxide catalyst having the gross composition $\text{Mo}_{12}\text{W}_2\text{Bi}_1\text{Co}_{5.5}\text{Fe}_3\text{Si}_{1.6}\text{K}_{0.08}\text{O}_x$ was introduced in each case in the stated form into the reaction tube.

10 The reaction temperatures and the selectivity of the reaction to give acrolein and acrylic acid or to give CO_2 are shown in each case in the Table below.

Example 1 (Comparison):

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The catalyst in the form of an annular unsupported catalyst having the dimensions: external diameter x height x internal diameter = 5 x 3 x 2 mm was introduced into the reaction tube.

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In this conventional reaction, the proportion of total combustion, expressed by the selectivity of the reaction of CO_x (4.8% or 6.5%), is relatively high.

25 **Example 2:**

A calcined catalyst of the abovementioned gross composition was milled, 100 g of this powder was then thoroughly mixed with 100 g of glycerol and the resulting suspension was then applied by immersion to the inner surface of a reaction tube having the abovementioned dimensions at room temperature. The tube was then heated at 300°C for two hours. The coating process was then repeated and, after coating
30 twice, a multimetal oxide catalyst layer (35 g of active material) was obtained.
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By using the catalyst according to the invention as a coating on the inner wall of the reaction tube, the

selectivity of the reaction with respect to acrolein and acrylic acid was substantially improved. Even at a reaction temperature (400°C) higher than that of Comparative Example 1, a higher selectivity with respect to acrolein and acrylic acid (95.6%) compared with a selectivity of only 92.3% at a lower reaction temperature of 360°C is achieved.

Example 3:

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In a tube coated according to Example 2, a stainless steel spiral having a wall width of 1.5 cm and a wall thickness of 2 mm was installed for inducing intense gas turbulence and was investigated.

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The gas mixing improved by installation of the stainless steel spiral leads to an improved selectivity of the reaction with respect to acrolein and acrylic acid.

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Example 4:

The spiral from Example 3 was coated analogously to the coating in Example 2 with a catalyst powder/glycerol mixture by immersion (10 g of active material on the spiral coils) and was tested.

By coating the stainless steel spiral with multimetal oxide catalyst, the selectivity is further substantially improved.

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Example 5:

100 g of conventional unsupported catalyst corresponding to Example 1 were installed in a tube which was coated analogously to Example 2 (35 g of active material on the inner surface of the tube), in the reactor exit. The bed height was 30 cm.

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By the combined use of the catalyst as a coating and simultaneously as an unsupported catalyst, a substantial improvement in the selectivity compared with the conventional use of the catalyst, as an unsupported catalyst, is achieved.

The improvement in selectivity achieved with the reaction tubes coated according to the invention leads to a substantial improvement in the cost-efficiency of industrial processes.

Example	Catalyst	Reaction temperature [°C]	Selectivity with respect to acrolein and acrylic acid [%]	Selectivity with respect to CO _x [%]
1	310 g of catalyst rings (5x3x2), conventional	325	95.0	4.8
1	310 g of catalyst rings (5x3x2), conventional	360	93.2	6.5
2	35 g of catalyst applied as coating to inner surface of tube	360	97.4	2.4
2	35 g of catalyst applied as coating to inner surface of tube	400	95.6	4.2
3	35 g of catalyst applied as coating to inner surface of tube	360	97.1	2.2

Example	Catalyst	Reaction temperature [°C]	Selectivity with respect to acrolein and acrylic acid [%]	Selectivity with respect to CO _x [%]
3	35 g of catalyst applied as coating to inner surface of tube	400	96.0	3.5
4	35 g of catalyst applied as coating to inner surface of tube and spiral coils (10 g of catalyst as coating)	360	97.8	2.0
4	35 g of catalyst applied as coating to inner surface of tube and spiral coils (10 g of catalyst as coating)	400	97.9	1.5

We claim:-

1. A metallic reaction tube having a catalytic coating, wherein the coating contains a multimetal oxide material which contains molybdenum and bismuth and is applied directly to the reaction tube.
2. A reaction tube as claimed in claim 1, wherein the multimetal oxide material contains molybdenum in an amount from 20 to 90, preferably from 30 to 80, particularly preferably from 40 to 70, % by weight, calculated as MoO_3 .
3. A reaction tube as claimed in claim 1 or 2, wherein the catalytic coating is applied to the inner wall of the tube.
4. A reaction tube as claimed in any of claims 1 to 3, wherein the catalytic coating has a coat thickness of from 10 to 100 μm , preferably from 20 to 500 μm , particularly preferably from 50 to 350 μm .
5. A tube-bundle reactor comprising reaction tubes as claimed in any of claims 1 to 4.
6. A tube-bundle reactor as claimed in claim 5, wherein a bed of unsupported or coated catalysts comprising multimetal oxide is introduced into the reaction tubes, preferably in their totality, in particular to a height of from 5 to 90%, preferably from 10 to 70%, especially from 20 to 50%, of the length of the reactor tube.
7. A tube-bundle reactor as claimed in either of claims 5 and 6, comprising a downstream second reactor, in particular a tube-bundle reactor, having a bed of unsupported or coated catalysts



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comprising multimetal oxide.

5 8. A process for the production of coated reaction tubes as claimed in any of claims 1 to 4 or of tube-bundle reactors as claimed in any of claims 5 to 7, which comprises the following steps:

10 (1) Preparation of solutions, emulsions and/or dispersions of elements and/or compounds of the elements present in the multimetal oxide catalyst and/or multimetal oxide catalyst precursor,

15 (2) if required, introduction of adhesion promoters, binders, viscosity regulators and/or pH regulators into the solutions, emulsions and/or dispersions,

20 (3) application of the solutions, emulsions and/or dispersions to the reaction tube or the reaction tubes of the tube-bundle reactor, preferably to their inner surface, preferably by spraying or immersion, and

25 (4) heating of the coated reaction tube, in the presence or absence of inert or reactive gases, to a temperature of from 20 to 1500°C, preferably from 200 to 400°C, for drying and, if required, sintering or calcining the multimetal oxide catalysts and/or multimetal oxide catalyst precursors.

30 9. A process for the preparation of (meth)acrolein and/or (meth)acrylic acid by catalytic gas-phase oxidation of C₁-C₆-alkanes, C₂-C₆-alkenes, C₁-C₆-alkanols and/or C₁-C₆-alkanals and/or precursors thereof using a reaction tube as claimed in any of claims 1 to 4 or a tube-bundle reactor as claimed
35 in any of claims 5 to 7.

