

Preparation of multimetal oxide materials

The present invention relates to a process for the preparation of
5 multimetal oxide materials of the formula I



where

10

A: is $MO_{12}V_aX^1_bX^2_cX^3_dX^4_eX^5_fX^6_gO_x$,

B: is $X^7_{12}Cu_hH_iO_y$,

15 X^1 : is W, Nb, Ta, Cr and/or Ce, preferably W, Nb and/or Cr,
 X^2 : is Cu, Ni, Co, Fe, Mn and/or Zn, preferably Cu, Ni, Co
and/or Fe,

X^3 : is Sb and/or Bi, preferably Sb,

X^4 : is Li, Na, K, Rb, Cs and/or H, preferably Na and/or K,

X^5 : is Mg, Ca, Sr and/or Ba, preferably Ca, Sr and/or Ba,

20 X^6 : is Si, Al, Ti and/or Zr, preferably Si, Al and/or Ti,

X^7 : is Mo, W, V, Nb and/or Ta, preferably Mo and/or W,

a: is from 1 to 8, preferably from 2 to 6,

b: is from 0.2 to 5, preferably from 0.5 to 2.5,

c: is from 0 to 23, preferably from 0 to 4,

25 d: is from 0 to 50, preferably from 0 to 3,

e: is from 0 to 2, preferably from 0 to 0.3,

f: is from 0 to 5, preferably from 0 to 2,

g: is from 0 to 50, preferably from 0 to 20,

h: is from 4 to 30, preferably from 6 to 24, particularly
30 preferably from 8 to 18,

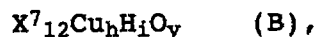
i: is from 0 to 20, preferably from 0 to 10,

x and y: are numbers which are determined by the valency and
frequency of the elements other than oxygen in I and

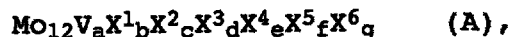
p and q: are numbers other than zero and whose ratio p/q is from
35 160:1 to 1:1, preferably from 20:1 to 1:1, particularly
preferably from 15:1 to 3:1,

in which a multimetal oxide material B

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in finely divided form is first formed separately (starting
material 1) and the preformed solid starting material 1 is then
incorporated into an aqueous solution of sources of the elements
45 Mo, V, X^1 , X^2 , X^3 , X^4 , X^5 and X^6 which contain the abovementioned
elements in the stoichiometry A



(starting material 2), in the desired molar ratio p:q, the resulting aqueous mixture is dried and the resulting precursor material is calcined at from 250 to 600°C, preferably from 300 to 450°C, before or after being shaped to give the desired catalyst geometry.

Multimetal oxide materials of the formula I are disclosed, for example, in DE-A 19528646 and are used as catalysts, for example in gas-phase catalytic oxidations of organic compounds, such as alkanes, alkanols, alkanals, alkenes and alkenols preferably of 3 to 6 carbon atoms (eg. propylene, acrolein, methacrolein, tert-butanol, the methyl ether of tert-butanol, isobutene, isobutane or isobutyraldehyde) to give olefinically unsaturated aldehydes and/or carboxylic acids, and the corresponding nitriles (ammoxidation, especially of propene to acrylonitrile or of isobutene or tert-butanol to methacrylonitrile).

DE-A 19528646 recommends carrying out the preparation of the multimetal oxide materials in the manner described at the outset, the incorporation of the solid starting material 1 into the aqueous starting material 2 being carried out in the embodiments at $\geq 80^\circ\text{C}$ in all cases. DE-A 19528646 does not contain further information regarding the temperature of incorporation.

The disadvantage of the abovementioned method of preparation in DE-A 19528646 is that, when the resulting multimetal oxide materials I are used as catalysts for the gas-phase catalytic oxidation of acrolein to acrylic acid, the selectivity of the acrylic acid formation is not completely satisfactory.

The preparation of multimetal oxide materials of the formula I is furthermore disclosed in EP-A 668 104.

The method of preparation in EP-A 668 104 is as described in DE-A 19528646. EP-A 668104 provides essentially no information regarding the temperature of incorporation of the solid starting material 1 into the aqueous starting material 2.

It is an object of the present invention to provide an improved process for the preparation of multimetal oxide materials I which does not have the abovementioned disadvantage.

We have found that this object is achieved by a process for the preparation of multimetal oxide materials I as described at the outset, wherein the incorporation of the solid starting material I

into the aqueous starting material 2 is carried out at $\leq 70^\circ\text{C}$. The temperature of incorporation is preferably $\leq 60^\circ\text{C}$, particularly preferably $\leq 40^\circ\text{C}$. As a rule, the incorporation is effected at room temperature, so that the temperature of incorporation is in general $\geq 0^\circ\text{C}$.

According to the invention, the finely divided starting material I advantageously consists of particles whose maximum diameter d_B (longest connecting line between two points on the surface of the particle and passing through the center of gravity of the particle) is from > 0 to $300\text{ }\mu\text{m}$, preferably from 0.1 to $200\text{ }\mu\text{m}$, particularly preferably from 0.5 to $50\text{ }\mu\text{m}$, very particularly preferably from 1 to $30\text{ }\mu\text{m}$. However, the particle diameter d_B can of course also be from 10 to $80\text{ }\mu\text{m}$ or from 75 to $125\text{ }\mu\text{m}$.

It is also advantageous if the starting material 1 to be used according to the invention has a specific surface area A_B (determined according to DIN 66131 by gas adsorption (N_2) by the Brunauer-Emmet-Teller (BET) method) of ≤ 20 , preferably ≤ 5 , very particularly preferably ≤ 1 , m^2/g . As a rule, A_B is $> 0.1\text{ m}^2/\text{g}$.

In principle, the starting material 1 may be used, according to the invention, in amorphous and/or crystalline form.

It is advantageous if the starting material 1 consists of crystallites of oxometallates or contains such oxometal crystallites which have the X-ray diffraction pattern and hence the crystal structure type of at least one of the following copper molybdates (the expression in brackets gives the source of the associated X-ray diffraction fingerprint) or if the starting material 1 consists of crystallites of these copper molybdates or contains such copper molybdate crystallites:

$\text{Cu}_4\text{Mo}_6\text{O}_{20}$ [A. Moini et al., Inorg. Chem. 25 (21) (1986), 3782 - 3785],

$\text{Cu}_4\text{Mo}_5\text{O}_{17}$ [index card 39-181 of the JCPDS-ICDD index (1991)],

$\alpha\text{-CuMoO}_4$ [index card 22-242 of the JCPDS-ICDD index (1991)],

$\text{Cu}_6\text{Mo}_5\text{O}_{18}$ [index card 40-865 of the JCPDS-ICDD index (1991)],

$\text{Cu}_{4-x}\text{Mo}_3\text{O}_{12}$ where x is from 0 to 0.25 [index cards 24-56 and 26-547 of the JCPDS-ICDD [sic] index (1991)],

$\text{Cu}_6\text{Mo}_4\text{O}_{15}$ [index card 35-17 of the JCPDS-ICDD index (1991)],

$\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$ [index card 36-405 of the JCPDS-ICDD index (1991)],

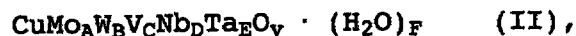
5 $\text{Cu}_3\text{Mo}_2\text{O}_9$ [index cards 24-55 and 34-637 of the JCPDS-ICDD index (1991)],

Cu_2MoO_5 [index card 22-607 of the JCPDS-ICDD index (1991)].

Multimetal oxide materials B which contain oxometallates or
10 consist thereof, which have the X-ray diffraction pattern and hence the crystal structure type of the following copper molybdate or which contain this copper molybdate itself or consist thereof are advantageous according to the invention:

15 CuMoO_4 -III having the wolframite structure according to Russian Journal of Inorganic Chemistry 36 (7) (1991), 927 - 928, Table 1.

Among these, those having the following stoichiometry II
20



where

25 $1/(A+B+C+D+E)$: is from 0.7 to 1.3, preferably from 0.85 to 1.15, particularly preferably from 0.95 to 1.05, very particularly preferably 1,

30 F : is from 0 to 1,

$B+C+D+E$: is from 0 to 1, preferably from 0 to 0.7, and

y is a number which is determined by the valency and frequency of the elements other than oxygen,

35 are preferred.

Particularly preferred among these are those having the stoichiometry III, IV or V:

40 $\text{CuMo}_A\text{W}_B\text{V}_C\text{O}_Y \quad (\text{III}),$

where

45

5

1/(A+B+C): is from 0.7 to 1.3, preferably from 0.85 to 1.15, particularly preferably from 0.95 to 1.05, very particularly preferably 1,

5 B + C: is from 0 to 1, preferably from 0 to 0.7, and

y is a number which is determined by the valency and frequency of the elements other than oxygen;

10 $\text{CuMo}_A\text{W}_B\text{O}_y$ (IV),

where

1/(A+B): is from 0.7 to 1.3, preferably from 0.85 to 1.15, particularly preferably from 0.95 to 1.05, very particularly preferably 1,

15

A and B: are each from 0 to 1 and

y is a number which is determined by the valency and frequency of the elements other than oxygen;

20

$\text{CuMo}_A\text{V}_C\text{O}_y$ (V),

where

25

1/(A+C): is from 0.7 to 1.3, preferably from 0.85 to 1.15, particularly preferably from 0.95 to 1.05, very particularly preferably 1,

30 A and C: are each from 0 to 1 and

y: is a number which is determined by the valency and frequency of the elements other than oxygen.

35 The preparation of such oxometallates or starting materials B is disclosed, for example, in EP-A 668 104.

Other suitable metal oxide materials B are those which [lacuna] oxometallates of the following stoichiometry VI

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$\text{CuMo}_A\text{W}_B\text{V}_C\text{Nb}_D\text{Ta}_E\text{O}_y$ (VI),

where

45

1/(A+B+C+D+E): is from 0.7 to 1.3, preferably from 0.85 to 1.15, particularly preferably from 0.95 to 1.05, very particularly preferably 1,

5 (B+C+D+E)/A: is from 0.01 to 1, preferably from 0.05 to 0.3, particularly preferably from 0.075 to 0.15, very particularly preferably 0.11, and

10 y: is a number which is determined by the valency and frequency of the elements other than oxygen,

having a structure type which is referred to as the HT copper molybdate structure and defined below by its X-ray diffraction pattern (fingerprint), represented by its most characteristic and
15 most intense diffraction lines in the form of interplanar spacings d [Å] independent of the wavelength of the X-rays used:

	6.79 ± 0.3
	3.56 ± 0.3
	3.54 ± 0.3
20	3.40 ± 0.3
	3.04 ± 0.3
	2.96 ± 0.3
	2.67 ± 0.2
	2.66 ± 0.2
25	2.56 ± 0.2
	2.36 ± 0.2
	2.35 ± 0.2
	2.27 ± 0.2
	2.00 ± 0.2
30	1.87 ± 0.2
	1.70 ± 0.2
	1.64 ± 0.2
	1.59 ± 0.2
	1.57 ± 0.2
35	1.57 ± 0.2
	1.55 ± 0.2
	1.51 ± 0.2
	1.44 ± 0.2

40 Where the multimetal oxide material B contains a mixture of different oxometallates or consists of such a mixture, a mixture of oxometallates having the wolframite and HT copper molybdate structure is preferred. The weight ratio of crystallites having the HT copper molybdate structure to crystallites having the
45 wolframite structure may be from 0.01 to 100, from 0.1 to 10, from 0.25 to 4 or from 0.5 to 2.

The preparation of oxometallates VI and starting materials B containing them is disclosed, for example, in DE-A 19528646.

In principle, multimetal oxide materials B suitable according to the invention can be prepared in a simple manner by producing, from suitable sources of their elemental constituents, a very intimate, preferably finely divided dry blend having a composition corresponding to their stoichiometry and calcining said dry blend at from 200 to 1000°C, preferably from 250 to 800°C, for several hours under inert gas or, preferably, in the air, it being possible for the duration of calcination to be from a few minutes to a few hours. The calcination atmosphere may additionally contain steam. Suitable sources for the elemental constituents of the multimetal oxide material B are those compounds which are already oxides and/or those compounds which can be converted into oxides by heating, at least in the presence of oxygen. In addition to the oxides, halides, nitrates, formates, oxalates, citrates, acetates, carbonates, amine complex salts, ammonium salts and/or hydroxides are particularly suitable as such starting compounds (compounds such as NH_4OH , $(\text{NH}_4)_2\text{CO}_3$, NH_4NO_3 , NH_4CHO_2 , CH_3COOH , $\text{NH}_4\text{CH}_3\text{CO}_2$ or ammonium oxalate which can decompose and/or can be decomposed at the latest during the subsequent calcination into compounds escaping in completely gaseous form may additionally be incorporated). The thorough mixing of the starting compounds for the preparation of multimetal oxide materials B can be carried out in dry or wet form. If it is effected in dry form, the starting compounds are advantageously used in the form of finely divided powders and are subjected to the calcination after mixing and, if required, compaction. However, the thorough mixing is preferably carried out in wet form. Usually, the starting compounds are mixed with one another in the form of an aqueous solution and/or suspension. Particularly intimate dry blends are obtained in the dry method described when exclusively dissolved sources of the elemental constituents are used as starting materials. A preferably used solvent is water. The aqueous material obtained is then dried, the drying process preferably being effected by spray drying of the aqueous mixture with outlet temperatures of from 100 to 150°C. The dried material is then calcined as described above.

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In another method of preparation of the multimetal oxide materials B, the thermal treatment of the mixture of the starting compounds used is carried out in an autoclave in the presence of steam at superatmospheric pressure, at from > 100 to 600°C. The pressure range typically extends to 500 atm, preferably to 250 atm. This hydrothermal treatment is particularly advantageously carried out in the temperature range from > 100 to

374.15°C (critical temperature of water) in which steam and liquid water coexist under the resulting pressures.

The multimetal oxide materials B which are obtainable as described
5 above and which may contain oxymetallates of an individual structure type or a mixture of oxometallates of different structure types or consist exclusively of oxometallates of an individual structure type or of a mixture of oxometallates of different structure type can be used, for example as such, as
10 solid starting material 1, if necessary after milling and/or classification to desired sizes.

For the preparation of the aqueous starting material 2 required according to the invention, suitable sources of the elemental
15 constituents are also those compounds which are already oxides and/or those compounds which can be converted into oxides by heating, at least in the presence of oxygen. In addition to the oxides, halides, nitrates, formates, oxalates, citrates, acetates, carbonates and/or hydroxides are particularly suitable
20 as such starting compounds (compounds such as NH_4OH , $(\text{NH}_4)_2\text{CO}_3$, NH_4HCO_3 , NH_4NO_3 , NH_4CHO_2 , CH_3COOH or $\text{NH}_4\text{CH}_3\text{CO}_2$ which can decompose and/or can be decomposed at the latest during the subsequent calcination into compounds escaping in completely gaseous form may additionally be incorporated). Particularly suitable starting
25 compounds of Mo, V, W and Nb are also their oxo compounds (molybdates, vanadates, tungstates and niobates) or the acids derived from these. This applies in particular to the corresponding ammonium compounds (ammonium molybdate, ammonium vanadate and ammonium tungstate).

30

For the preparation of an aqueous solution required according to the invention as starting material 2, it is as a rule necessary, starting from abovementioned sources of the elemental constituents, to employ elevated temperatures. As a rule,
35 temperatures of $\geq 60^\circ\text{C}$, in general $\geq 70^\circ\text{C}$, but usually $\leq 100^\circ\text{C}$ are used. The above and the following apply in particular when ammonium heptamolybdate tetrahydrate [$\text{AHM} = (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$] is used as the Mo elemental source and/or ammonium metavanadate [$\text{AMV} = \text{NH}_4\text{VO}_3$] as the vanadium source. The conditions are
40 particularly difficult when the element W is part of the aqueous starting material 2 and ammonium paratungstate heptahydrate [$\text{APW} = (\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 7 \text{H}_2\text{O}$] is used as the starting compound of the relevant aqueous solution, in addition to at least one of the two abovementioned elemental sources.

45

We have found, surprisingly, that aqueous solutions prepared at elevated temperatures as starting material 2 are usually stable during and after the subsequent cooling below the dissolution temperature, even in the case of elemental Mo contents of $\geq 10\%$ by weight and cooling temperatures down to 20°C or lower (generally not $< 0^\circ\text{C}$), based on the aqueous solution, ie. no solid is precipitated during or after the cooling of the aqueous solution. As a rule, the abovementioned statement is also true in the case of Mo contents of up to 20% by weight, based on the aqueous solution.

Usually, the Mo content of such aqueous solutions cooled to 20°C or below (generally not below 0°C) and suitable as starting material 2 is not more than 35% by weight, based on the solution.

The above finding, which for the first time permits the novel procedure, is due to the fact that, on dissolution at elevated temperatures, compounds of the relevant elements which have high water solubility are evidently formed. This concept is supported by the fact that the residue obtainable from such an aqueous solution by drying (eg. spray drying) has a correspondingly increased solubility in water (even at the corresponding low temperatures).

We have also surprisingly found that, with the use of aqueous solutions prepared as starting material 2, multimetal oxide materials I prepared according to the invention (for the preparation of which the finely divided starting material 1 is incorporated at a low temperature) leads to higher acrylic acid selectivities, in particular in the partial gas-phase oxidation of acrolein to acrylic acid.

According to the invention, it is therefore advantageous to proceed as follows. An aqueous solution suitable as starting material 2 is produced at $T_L \geq 60^\circ\text{C}$ (for example at up to 65°C , or at up to 75°C , or at up to 85°C , or at up to 95°C or at $\leq 100^\circ\text{C}$). The finely divided solid starting material 1 is then incorporated into this aqueous solution, after cooling to a temperature $T_E < T_L$. Frequently, T_L is $> 70^\circ\text{C}$ and T_E is $\leq 70^\circ\text{C}$. If slightly lower dissolution rates and lower solids contents are accepted, however, $T_L \geq 60^\circ\text{C}$ is also possible.

The incorporation of the solid starting material 1, prepared beforehand, into the aqueous starting material 2 is usually carried out by adding the starting material 1 to the aqueous starting material 2 cooled as described above and then effecting mechanical mixing, for example with the use of stirring or

dispersing aids, over a period of from a few hours to several days, preferably several hours. As stated above, it is particularly advantageous according to the invention if the incorporation of the solid starting material 1 into the aqueous starting material 2 is carried out at $\leq 70^{\circ}\text{C}$, preferably $\leq 60^{\circ}\text{C}$, particularly preferably $\leq 40^{\circ}\text{C}$. As a rule, the temperature of incorporation is $\geq 0^{\circ}\text{C}$.

Furthermore, it is particularly advantageous according to the invention if the solid starting material 1 is incorporated into an aqueous starting material 2 whose pH at 25°C is from 4 to 7, preferably from 5 to 6.5. The latter can be achieved, for example, by adding one or more pH buffer systems to the aqueous starting material 2. Suitable as such is, for example, the addition of ammonia and acetic acid and/or formic acid or the addition of ammonium acetate and/or ammonium formate. With regard to the abovementioned intended use, it is of course also possible simultaneously to employ ammonium carbonate.

The aqueous mixture obtained on incorporating the starting material 1 into the aqueous starting material 2 is usually dried by spray-drying. Advantageously, outlet temperatures of from 100 to 150°C are established. Spray drying may be carried out by either the cocurrent or the countercurrent method.

When the precursor materials obtained in the abovementioned spray drying are used for preparing catalysts for the gas-phase catalytic oxidation of acrolein to acrylic acid, the shaping to the desired catalyst geometry is preferably effected by application to preformed inert catalyst carriers, where the application may be effected before or after the final calcination. As a rule, the relevant precursor material is calcined before the coating of the carrier. As a rule, coating of the carriers for the preparation of the coated catalysts is carried out in a suitable rotatable container, as disclosed, for example, in DE-A 2909671 or EP-A 293859. For coating the carriers, the powder material to be applied can advantageously be moistened and, after the application, dried again, for example by means of hot air. The coat thickness of the powder material applied to the carrier is advantageously from 50 to $500\text{ }\mu\text{m}$, preferably from 150 to $250\text{ }\mu\text{m}$.

The carrier materials used may be conventional porous or nonporous aluminas, silica, thorium dioxide, zirconium dioxide, silicon carbide or silicates, such as magnesium silicate or aluminum silicate. The carriers may have a regular or irregular shape, carriers having a regular shape and well developed surface

roughness, for example spheres or hollow cylinders, being preferred. Among these in turn, spheres are particularly advantageous. The use of essentially nonporous spherical steatite carriers which have a rough surface and whose diameter is from 1 5 to 8 mm, preferably from 4 to 5 mm, is particularly advantageous.

The precursor material obtained in the spray drying in the course of the novel process can also be used for preparing unsupported catalysts. In this context, the precursor material is compacted 10 (for example by pelleting or extrusion) to give the desired catalyst geometry before or after the calcination, and, if required, the conventional assistants, for example graphite or stearic acid as lubricant and/or mold release agent and reinforcing agents, such as microfibers of glass, asbestos, 15 silicon carbide or potassium titanate, may be added. Preferred unsupported catalyst geometries are hollow cylinders having an external diameter and a length of from 2 to 10 mm and a wall thickness of from 1 to 3 mm.

20 The calcination of the precursor materials prepared according to the invention in the abovementioned spray drying to give the actual catalytically active multimetal oxide materials is carried out at from 250 to 600°C, preferably from 300 to 450°C, regardless whether it is effected before or after shaping. The calcination 25 can be carried out under inert gas (eg. N₂), a mixture of inert gas and oxygen (eg. air), reducing gases, such as hydrocarbons (eg. methane), aldehydes (eg. acrolein) or ammonia, or under a mixture of O₂ and reducing gases (for example all of the abovementioned ones), as described, for example, in DE-A 4335973. 30 In a calcination under reducing conditions, however, it should be ensured that the metallic constituents are not reduced to the element. The calcination is therefore advantageously carried out under an oxidizing atmosphere. The duration of the calcination is as a rule a few hours and usually decreases with increasing 35 calcination temperature.

The multimetal oxide materials I obtainable according to the invention are particularly suitable as catalysts having high selectivity (at a given conversion) for the gas-phase catalytic 40 oxidation of acrolein to acrylic acid. Usually, acrolein which was produced by the catalytic gas-phase oxidation of propene is used in the process. As a rule, the acrolein-containing reaction gases of this propene oxidation are used without intermediate purification. Usually, the gas-phase catalytic oxidation of 45 acrolein is carried out as a heterogeneous fixed-bed oxidation in tube-bundle reactors. Oxygen, advantageously diluted with inert gases (for example in the form of air), is used in a manner known

per se as the oxidizing agent. Suitable diluent gases are, for example, N_2 , CO_2 , a hydrocarbon, recycled reaction exit gases and/or steam. As a rule, an acrolein : oxygen : steam : inert gas volume ratio of 1 : (1 to 3) : (0 to 20) : (3 to 30), preferably 5 of 1 : (1 to 3) : (0.5 to 10) : (7 to 18) is established in the acrolein oxidation. The reaction pressure is in general from 1 to 3 bar and the total space velocity is preferably from 1000 to 3500 l (s.t.p.)/(l.h). Typical multitube fixed-bed reactors are described, for example, in DE-A 28 30 765, DE-A 22 01 528 or 10 US-A 3 147 084. The reaction temperature is usually chosen so that the acrolein conversion is above 90%, preferably above 98%, in a single pass. Usually, reaction temperatures of from 230 to 330°C are required for this.

15 In addition to the gas-phase catalytic oxidation of acrolein to acrylic acid, the novel products are however also capable of catalyzing the gas-phase catalytic oxidation of other organic compounds, in particular other alkanes, alkanols, alkanals, alkenes and alkenols, preferably of 3 to 6 carbon atoms (eg. 20 propylene, methacrolein, tert-butanol, methyl ether of tert-butanol, isobutene, isobutane or isobutyraldehyde), to olefinically unsaturated aldehydes and/or carboxylic acids, and the corresponding nitriles (ammoxidation, especially of propene to acrylonitrile and of isobutene or tert-butanol to 25 methacrylonitrile). The preparation of acrolein, methacrolein and methacrylic acid may be mentioned by way of example. However, they are also suitable for the oxidative dehydrogenation of olefinic compounds.

30 In this publication, conversion, selectivity and residence time are defined as follows, unless stated otherwise:

35	Conversion C of acrolein (%) =	$\frac{\text{number of moles of converted acrolein}}{\text{number of moles of acrolein used}} \times 100$
40	Selectivity S of the acrylic acid formation =	$\frac{\text{number of moles converted to acrylic acid}}{\text{number of moles of converted acrolein}} \times 100$
45	Residence time (sec) =	$\frac{\text{empty reactor volume filled with catalyst (l)}}{\text{synthesis gas throughput (l (s.t.p.)/h)}} \times 3600$

Examples

Comparative Example 1:

5 732.7 g of ammonium heptamolybdate tetrahydrate (82.5% by weight of MoO_3) and 146.5 g of ammonium metavanadate (75.2% by weight of V_2O_5) were dissolved in 5430 g of water in the course of a few minutes at 50°C while stirring. 126.3 g of ammonium paratungstate heptahydrate (89.0% by weight of WO_3) were then added and the
10 suspension was stirred for a further 3 days at 50°C . It was not possible to achieve complete dissolution, even after the 3 days.

Example 1:

15 732.7 g of ammonium heptamolybdate tetrahydrate (82.5% by weight of MoO_3), 146.5 g of ammonium metavanadate (75.2% by weight of V_2O_5) and 126.3 g of ammonium paratungstate heptahydrate (89.0% by weight of WO_3) were dissolved in 5430 g of water in succession at 95°C while stirring. Complete dissolution was achieved after only
20 1 hour. The clear orange solution obtained was stirred for a further 24 hours at 95°C and remained unchanged. The clear, orange solution obtained was then cooled to 25°C . The orange solution remained precipitate-free and clear for 24 hours at 25°C .

25 Example 2:

126.3 g of ammonium paratungstate heptahydrate (89.0% by weight of WO_3), 146.5 g of ammonium metavanadate (75.2% by weight of V_2O_5) and 732.7 g of ammonium heptamolybdate tetrahydrate (82.5%
30 by weight of MoO_3) were dissolved in 5430 g of water in succession at 95°C while stirring. Complete dissolution was achieved after only 0.5 hours.

The temperature of the solution was then reduced to 40°C . The
35 solution remained clear and precipitate-free.

Example 3:

Starting material 1:
40

219.8 g of ammonium heptamolybdate tetrahydrate (82.5% by weight of MoO_3) and 328.25 g of ammonium paratungstate heptahydrate (89.0% by weight of WO_3) were dissolved in 5 l of water at 95°C while stirring (solution A). 3 l of water and 445.0 g of a 25%
45 strength by weight aqueous ammonia solution were added to 482.34 g of copper acetate hydrate (41.6% by weight of CuO) and stirring was carried out for 15 minutes at 25°C , a deep blue solution being

obtained (solution B). The solution B was then stirred into the solution A at 95°C, the temperature of the solution A not falling below 80°C. The resulting suspension C was stirred for a further hour at 80°C and had a pH (glass electrode) of 8.5. The

5 suspension C was spray-dried at an inlet temperature of 310°C and an outlet temperature of 110°C. The resulting light green spray powder was kneaded with water (200 g of water per 1 kg of spray powder) and molded in an extruder at 50 bar to give 6 mm thick extrudates (about 1 cm long). These extrudates were dried for

10 16 hours at 110°C in air. The calcination of the extrudates was then carried out in air. The material to be calcined was introduced into a furnace at 300°C, left at this temperature for 30 minutes, heated to 750°C in the course of 1 hour and left at this temperature of 750°C for 1 hour. The resulting product had a

15 reddish brown color and, after milling in a centrifugal mill from Retsch, Germany, a specific surface area according to DIN 66 131 of 0.8 m²/g and the composition Cu₁₂Mo₆W₆O₄₈. With the use of CuKα radiation (Siemens D-5000 diffractometer, 40 kV, 30 mA, with automatic scatter and counter aperture and Peltier detector), the

20 resulting crystalline powder of the composition Cu₁₂Mo₆W₆O₄₈ gave a powder X-ray diffraction pattern which showed a superposition of the wolframite fingerprint on the HT copper molybdate fingerprint, ie. it had a two-phase structure. According to the line intensities, the two structure types were present in the

25 ratio of about 90 (wolframite structure) : 10 (HT copper molybdate structure).

Starting material 2

30 732.7 g of ammonium heptamolybdate tetrahydrate (82.5% by weight of MoO₃), 146.5 g of ammonium metavanadate (75.2% by weight of V₂O₅) and 126.3 g of ammonium paratungstate heptahydrate (89.0% by weight of WO₃) were dissolved in 5430 g of water in succession at 95°C. The aqueous solution (starting material 2) was thus based on

35 the following elemental stoichiometry:



Active material:

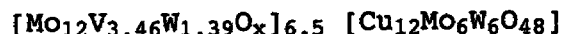
40

The clear, orange solution (active material 2) obtained was then cooled to 25°C. 172.7 g of starting material 1 were stirred into starting material 2 cooled to 25°C, so that the molar ratio of the abovementioned stoichiometric units was 1 (starting material 1) to

45 6.5 (starting material 2). Thereafter, 150.0 g of ammonium acetate were furthermore stirred into the aqueous suspension, the resulting suspension was stirred for a further hour at 25°C and

15

the aqueous mixture was then spray-dried. The spray powder was then kneaded with a mixture of 70% by weight of water and 30% by weight of acetic acid (0.35 kg of liquid by 1 kg of spray powder). The kneaded material obtained was dried for 16 hours at 110°C in
 5 air. The comminuted kneaded material was calcined in a rotating tube fed with an oxygen/nitrogen mixture. 700 g of material to be calcined were introduced into the cylindrical calcination chamber (length: 51 cm, internal diameter: 12.5 cm) of the rotating tube. During the entire calcination process, a mixture comprising 10 l
 10 (s.t.p.)/h of air and 200 l (s.t.p.)/h of nitrogen and preheated to the calcination temperature was passed through the calcination chamber of the rotating tube. During the calcination, the kneaded material was first heated to 210°C in the course of 20 minutes, then heated to 400°C in the course of 5 hours and then kept at
 15 this temperature for 3 hours. The resulting catalytically active material had the following gross stoichiometry:



20 As before, the X-ray diffraction pattern of the active material obtained contained the superposition of the wolframite structure type and HT copper molybdate structure type. After the calcined active material had been milled, it was used to coat nonporous steatite spheres having a rough surface and a diameter of from 4
 25 to 5 mm in a rotating drum in an amount of 50 g of active powder per 200 g of steatite spheres, with simultaneous addition of 18 g of water. The coated catalyst obtained was then dried with air at 110°C.

30 Example 4:

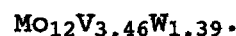
Starting material 1:

The starting material 1 from Example 3 was used as starting
 35 material 1.

Starting material 2:

732.7 g of ammonium heptamolybdate tetrahydrate (82.5% by weight
 40 of MoO_3), 146.5 g of ammonium metavanadate (75.2% by weight of V_2O_5) and 126.3 g of ammonium paratungstate heptahydrate (89.0% by weight of WO_3) were dissolved in 5430 g of water in succession at 95°C. The aqueous solution (starting material 2) was thus based on the following elemental stoichiometry:

45



Active material:

The clear, orange solution obtained (starting material 2) was then cooled to 25°C and 116.9 g of acetic acid and 132.3 g of ammonia solution (25% by weight of ammonia in water) were added to it in succession. 172.7 g of the starting material 1 were stirred into the buffered starting material 2 cooled to 25°C, so that the molar ratio of the abovementioned stoichiometric units was 1 (starting material 1) to 6.5 (starting material 2). The suspension obtained was stirred for a further hour at 25°C. The aqueous mixture obtained was then spray-dried and was further processed as in Example 3.

Comparative Example 2:

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The procedure was as in Example 3. In contrast to that example, however, the starting material 1 was stirred into the aqueous starting material 2 at 95°C and the resulting suspension was stirred for a further hour at 95°C after the addition of ammonium acetate.

Example 5:

The multimetal oxide catalysts prepared in Examples 3 and 4 and in Comparative Example 2 were introduced into a tubular reactor (V2A stainless steel, 25 mm internal diameter, 2000 g catalyst bed, salt bath heating) and fed with a gaseous mixture having the composition

5% by volume of acrolein,
7% by volume of oxygen,
10% by volume of steam and
78% by volume of nitrogen

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at reaction temperatures of from 250 to 270°C with the use of a residence time of 2.0 seconds. In all cases, the salt bath temperature was set so that, after the end of forming, a single pass resulted in a uniform acrolein conversion C of 99%. The product gas mixture flowing out of the reactor was analyzed by gas chromatography. The results for the selectivity of the acrylic acid formation using the various catalysts are shown in the table below.

Catalyst	S %
Example 3	96.3
Example 4	96.4

Comparative Example 2 17
96.0

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We claim:

1. A process for the preparation of multimetal oxide materials
5 of the formula I



where:

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A: is $Mo_{12}V_aX^1_bX^2_cX^3_dX^4_eX^5_fX^6_gO_x$,

B: is $X^7_{12}Cu_hH_iO_y$,

15

X^1 : is W, Nb, Ta, Cr or Ce,

X^2 : is Cu, Ni, Co, Fe, Mn or Zn,

X^3 : is Sb and/or Bi,

X^4 : is Li, Na, K, Rb, Cs or H,

X^5 : is Mg, Ca, Sr or Ba,

X^6 : is Si, Al, Ti or Zr,

20

X^7 : is Mo, W, V, Nb or Ta,

a: is from 1 to 8,

b: is from 0.2 to 5,

c: is from 0 to 23,

d: is from 0 to 50,

25

e: is from 0 to 2,

f: is from 0 to 5,

g: is from 0 to 50,

h: is from 4 to 30,

i: is from 0 to 20,

30

x and y: are numbers which are determined by the valency and frequency of the elements other than oxygen in I and

p and q: are numbers other than zero and whose ratio p/q is from 160:1 to 1:1,

35

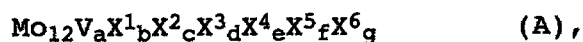
in which a multimetal oxide material B



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in finely divided form is first formed separately (starting material 1) and the preformed solid starting material 1 is then incorporated into an aqueous solution of sources of the elements Mo, V, X^1 , X^2 , X^3 , X^4 , X^5 and X^6 which contain the abovementioned elements in the stoichiometry A

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- (starting material 2), in the desired molar ratio p:q, the resulting aqueous mixture is dried and the resulting precursor material is calcined at from 250 to 600°C, before or after being shaped to give the desired catalyst geometry, wherein the preformed solid starting material 1 is incorporated into the aqueous starting material 2 at $\leq 70^\circ\text{C}$.
2. A process as claimed in claim 1, wherein the preformed solid starting material 1 is incorporated into the aqueous starting material 2 at $\leq 60^\circ\text{C}$.
3. A process as claimed in claim 1, wherein the preformed solid starting material 1 is incorporated into the aqueous starting material 2 at $\leq 40^\circ\text{C}$.
4. A multimetal oxide material obtainable by a process as claimed in any of claims 1 to 3.
5. An aqueous solution which contains the elements Mo, V, X^1 , X^2 , X^3 , X^4 , X^5 and X^6 in the stoichiometry $\text{Mo}_{12}\text{V}_a\text{X}^1_b\text{X}^2_c\text{X}^3_d\text{X}^4_e\text{X}^5_f\text{X}^6_g$ in solution, the variables having the meanings as claimed in claim 1, obtainable by dissolving sources of the abovementioned elements in water at $T_L \geq 60^\circ\text{C}$ and then cooling the aqueous solution to a temperature $T_E < T_L$.
6. An aqueous solution as claimed in claim 5, wherein T_L is $> 70^\circ\text{C}$ and T_E is $\leq 70^\circ\text{C}$.
7. An aqueous solution as claimed in claim 5, wherein T_L is $> 80^\circ\text{C}$ and T_E is $\leq 80^\circ\text{C}$.
8. An aqueous solution as claimed in any of claims 5 to 7, wherein its Mo content is from 10 to 35% by weight, based on the aqueous solution.
9. A solid obtainable by drying an aqueous solution as claimed in any of claims 5 to 8.
10. A process for the preparation of acrylic acid by gas-phase catalytic oxidation of acrolein, wherein the catalyst used is a multimetal oxide material as claimed in claim 4.