

DESCRIPTION

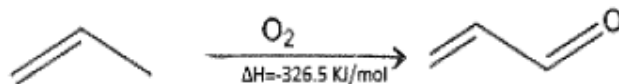
TITLE: Bismuth molybdate-based catalyst, process for the production thereof and use of this catalyst in the oxidation of propene to acrolein

The present invention concerns a method for preparing a multiphase mixed-oxide catalyst based on bismuth molybdate, a catalyst and a catalytic system obtained in this manner and the uses of these in different oxidation reactions.

The performances of the catalyst or of the catalytic system according to the invention are set out hereinafter in the controlled oxidation reaction of propene into acrolein. These are not restricted thereto and are interesting in particular in the oxidative dehydrogenation of butene into butadiene, the oxidation of isobutylene into methacrolein, the ammoxidation of propene into acrylonitrile and the ammoxidation of isobutylene into methacrylonitrile. All these well-known reactions are implemented on an industrial scale as they supply source monomers for the production of many polymers and precursors that are essential in organic synthesis. For this reason, they are continuously the object of researches aiming at improving their performances and reducing their ecological impact.

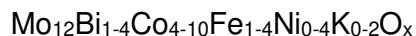
The controlled oxidation of propene that is represented hereinbelow leads to acrolein which is an intermediate for the synthesis of methionine and derivatives thereof, widely used in animal nutrition.

[Chem 1]



It is performed in the presence of a multiphase mixed-oxide catalyst, composed by at least four metallic elements: molybdenum and bismuth, which form the selective phases of bismuth molybdate, and a combination of metals in the oxidation state +2 (in general Ni or Co) and the oxidation state +3 (in general iron) and molybdenum which form phases that strongly enhance the catalytic activity by promoting the re-oxidation of the catalyst. Thus, it meets the minimum formula $\text{Mo}(\text{Co}/\text{Ni})\text{FeBiO}$ which is completed by various elements present as doping elements and/or in the form of oxides or molybdate, in order to improve the properties of the catalyst, such as selectivity, thermal stability, mechanical stability...

The document US2019/076829A1 describes such a catalyst and, *inter alia*, a catalyst meeting the following formula:



as well as a method for preparing it comprising the following steps:

an aqueous mixture of the precursors of the elements of the catalyst is prepared in proper contents so as to reach the stoichiometry,

after setting of the pH of the mixture to 5.5-8.5, said precursors are reacted
5 through a hydrothermal reaction in an autoclave at a temperature from 100°C to 600°C, for 5.5 hours to 48.5 hours, and then

the catalyst is retrieved.

Such a preparation requiring long reaction times, the authors have developed a method for producing a catalyst of the aforementioned type, by replacing the
10 hydrothermal reaction hereinabove with a microwave-assisted hydrothermal reaction. They have discovered that, while allowing reducing the reaction duration considerably, the obtained catalyst has unexpected characteristics, conferring better properties thereon, in particular a higher reactivity.

Thus, the invention concerns a method for producing a multiphase mixed-
15 oxide catalyst comprising at least one active phase based on bismuth molybdate and one co-catalyst based on iron molybdate and at least one amongst the two elements cobalt and nickel, said method comprising the following steps:

preparing a mixture of the precursors of said mixed oxides in a solvent,

making said precursors react through a microwave-assisted hydrothermal
20 reaction, and

isolating the mixed oxides to obtain the catalyst.

By microwaves according to the invention, it should be understood intermediate radiations between infrared and radio waves, namely waves whose frequency is comprised between 800 and 3000 MHz. In practice, since all
25 wavelengths are not authorized, preference will be given, yet without the invention being restricted thereto, to domestic microwaves used in industrial applications with a vacuum wavelength of about 12 cm, namely a frequency of about 2450 MHz, as well as microwaves used essentially in industrial applications, with a vacuum wavelength of about 33 cm, namely a frequency of about 915 MHz.

30 The method is described hereinafter in more details, the following features may be considered separately or in any combination.

According to a particular implementation of the method of the invention, said precursors are reacted through a microwave-assisted hydrothermal reaction in two steps, namely: a first microwave-assisted hydrothermal reaction and a second
35 microwave-assisted hydrothermal reaction, between which the pH of the reaction mixture obtained from the first microwave-assisted hydrothermal reaction is set to 8-8.5.

More specifically, in a first synthesis step, said precursors are added and reacted through a first microwave-assisted hydrothermal reaction, and in a second synthesis step, the pH of the reaction medium is set preferably to a value of 8-8.5, and a second microwave-assisted hydrothermal reaction is performed, and then the
 5 microwave catalyst is isolated.

The microwave-assisted hydrothermal reaction(s) is/are preferably performed at a temperature which does not exceed 300°C, advantageously from 150°C to 240°C.

As said before, the reaction time is significantly shortened and if the
 10 microwave-assisted hydrothermal reaction(s) could be carried out over a time period from 2 minutes to 10 hours, within a few hours, and even only a few minutes, the reaction may be almost complete.

Optionally, the catalyst prepared according to the method of the invention has the following features, which may be considered separately or in any combination:

15 it further comprises molybdenum oxide;

it is supported; in the method of the invention, the addition of one or several support material(s), such as silica, alumina, their mixtures, is advantageously performed before the microwave-assisted hydrothermal reaction(s); of course, an unsupported catalyst obtained according to the method of the invention may be
 20 supported afterwards according to any technique well known to those skilled in the art;

the active phase of the catalyst meets the following stoichiometry $\text{Bi}_x\text{Mo}_y\text{O}_z$ where $2 > x/y > 0.5$ and z is comprised between 6 and 12; still preferably this stoichiometry is selected amongst $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, $\text{Bi}_2\text{Mo}_2\text{O}_9$ and Bi_2MoO_6 ;

25 the active phase of the catalyst is activated by at least one alkali metal, preferably at least potassium; in an advantageous production way, only the active phase of the catalyst is activated by one or several alkali metal(s), such as potassium;

the co-catalyst meets the following stoichiometry $\text{Fe}_x\text{Co}_{1-x}\text{MoO}_4$ where x is a decimal number such that $0 < x < 1$, preferably such that $0.5 \leq x \leq 0.9$;

the catalyst meets the formula $\text{Mo}_m\text{Co}_n\text{Ni}_p\text{Fe}_q\text{Bi}_r\text{M}_s$ where M is an alkali metal, m , n , p , q , r and s are natural or decimal numbers, with m varying from 1 to 5, n and p varying independently of one another from 0 to 1 with $n+p$ different from 0, $0 < q \leq 1$, $0 < r \leq 3$ and $0 < s \leq 0.2$.

35 The invention also concerns the catalyst obtained in this manner.

In a particular implementation of the method of the invention:

a mixture of the precursors of the active phase in a solvent, on the one hand, and a mixture of the precursors of the co-catalyst in the same solvent or in another solvent, on the other hand, are prepared;

the precursors of the active phase and the precursors of the co-catalyst are
5 reacted separately, through a microwave-assisted hydrothermal reaction;

the active phase and the co-catalyst, respectively, are isolated; and

the active phase and the co-catalyst are assembled to obtain the catalyst.

Preferably, the mixture(s) of the precursors of the mixed oxides is/are obtained
in one or more of the solvents selected from water, organic solvents and any
10 combination of said organic solvents together or with water.

According to this implementation, the catalyst may be supported, said method
then comprising the addition of one or several support material(s), and/or the catalyst
may comprise molybdenum oxide, said method also comprising the addition of
molybdenum oxide, the addition of said support material(s) and/or of the
15 molybdenum oxide being carried out during the synthesis or the assembly of the
active phase and of the co-catalyst to obtain the catalyst. The molybdenum oxide
allows, on the one hand, compensating for the loss of molybdenum over time which
vaporizes thereby keeping the active phase and the co-catalyst in an optimum state
and, on the other hand, wetting the active phase and suppressing non-selective sites.
20 Of course, any other phase allowing improving the properties of the catalyst may be
added.

Each of the active phase and the co-catalyst, which may comprise any other
phase mentioned before, is generally obtained in the form of a powder. The
assembly thereof in order to obtain the catalyst may be done by any means enabling
25 the most complete amalgam possible. Thus, it may be performed by co-grinding or
any other compounding technique. Also at this step, any other phase or one or
several support material(s) may be added.

As indicated before, this method allows producing a mixed and multiphase
oxides catalyst which has proven to be effective in many catalytic reactions,
30 including: the oxidation of propene into acrolein, the oxidative dehydrogenation of
butene into butadiene, the oxidation of isobutylene into methacrolein, the
ammoxidation of propene into acrylonitrile and the ammoxidation of isobutylene into
methacrylonitrile.

The invention also concerns a catalytic system comprising separately at least
35 one active phase based on bismuth molybdate and one co-catalyst based on iron
molybdate and at least one amongst cobalt and nickel. To be used, the separated
phases are assembled as indicated before, for example by co-grinding.

This catalytic system which may be obtained according to the above-described method, comprises the following advantageous features, considered separately or in any combination:

the active phase meets the following stoichiometry $\text{Bi}_x\text{Mo}_y\text{O}_z$ where $2 > x/y > 0.5$ and z is comprised between 6 and 12; preferably this stoichiometry is selected amongst the following ones: $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, $\text{Bi}_2\text{Mo}_2\text{O}_9$ and Bi_2MoO_6 ;

the active phase is activated by at least one alkali metal, preferably at least potassium; advantageously, only this phase is activated by an alkali metal;

the co-catalyst meets the following stoichiometry $\text{Fe}_x\text{Co}_{1-x}\text{MoO}_4$ where x is a decimal number such that $0 < x < 1$, preferably such that $0.5 \leq x \leq 0.9$;

the active phase content is lower than or equal to 50 weight% with respect to the weight of the catalytic system, preferably it varies from 10% to 45%.

The invention also concerns any use of a catalytic system as defined hereinabove, in particular for at least one amongst the following catalytic reactions: the oxidation of propene into acrolein, the oxidative dehydrogenation of butene into butadiene, the oxidation of isobutylene into methacrolein, the ammoxidation of propene into acrylonitrile and the ammoxidation of isobutylene into methacrylonitrile.

In order to illustrate the implementations of the different objects of the invention, some terms/expressions are defined.

By mixture of the precursors of mixed oxides in a solvent, it should be understood in particular a solution or a suspension of said precursors in the solvent.

By isolation of the catalyst, or of any of its phases, in particular the active phase or the co-catalyst, it should be understood all treatment operations well known to those skilled in the art, such as retrieval from the liquid hydrothermal reaction medium, washing, drying, and any other treatment leading to the separation of the catalyst or of any of its phases, for the use thereof in a catalytic reaction.

In the following examples, the activity of catalysts of the invention and of a catalytic system of the invention is compared with that of a so-called industrial catalyst, that is to say prepared by calcination. The production method thereof was as follows:

Ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ has been used as a molybdenum precursor, whereas all of the other metals other than cations have been added in the form of nitrates. Since the solubility of the precursors in water is very high, the desired concentration ranges have been easy to obtain. Besides, since bismuth nitrate is immediately hydrolyzed into bismuth oxynitrate which is not soluble in water, $\text{Bi}_5\text{O}(\text{OH})_9(\text{NO}_3)_4$, and in order to promote the complete dissolution of bismuth which is barely soluble in water, a first solution has been prepared by dissolving 2g of tartaric acid in 100 ml of demineralized water that has been acidified beforehand with

1.5 ml of nitric acid (65 %). After the addition of bismuth nitrate, the solution has been heated to 60°C and kept under stirring for 30 min, until a colorless and clear solution is obtained. The addition of iron, cobalt and potassium in the form of nitrate has been executed in this order and each new salt has been added only after the complete dissolution of the previous one. Finally, the solutions 1 and 2 have been mixed under stirring and kept at 60°C for 3 hours. The resulting suspension has been completely evaporated in a furnace at 120°C. Finally, the obtained product has been calcined at 350°C for 2 hours to decompose the residual nitrates and then heated to 500°C at the rate of 5°C/min and kept at this temperature for 2 hours.

Example 1: Synthesis of a catalyst of the invention through a microwave-assisted hydrothermal reaction

The prepared catalyst meets the formula BiMoFeCoK , it has been produced as follows:

Bismuth acetate (or nitrate), iron nitrate and cobalt (or/and nickel) nitrate have been dissolved in 10 ml of H_2O so as to form the solution 1. Next, a stoichiometric amount of ammonium heptamolybdate has been dissolved in 10 ml of H_2O so as to form the solution 2. Afterwards, the solution 1 has been added slowly to the solution 2 so as to form a suspension, which has been kept under stirring for 1 hour. The pH of the mixture has been set to 1.8 by the supplemental HNO_3 or NH_4OH . Then, the suspension has been heated up to 150°C by irradiation with microwaves and kept at this temperature for 10 minutes in a first step. Once the first step is completed, KOH is added and the mixture is basified to pH 8.5 by adding ammonia 32%. Then, the suspension has been heated up to 200°C by irradiation with microwaves and kept at this temperature for 30 minutes. The obtained solid has been retrieved by centrifugation, washed twice with 10 ml of H_2O and once with 10 ml of ethanol and finally dried for 16 hours at 120°C.

The following variations have been tested: solvents, pH, reaction time (2 minutes to 96 h), irradiation temperature (150-240°C), stoichiometry $\text{Bi}_x\text{Fe}_y\text{Co}_z\text{Ni}_c\text{Mo}_b\text{K}_a$ with $0 \leq a, b, c, x, y, z \leq 15$.

An implementation of the method is represented in the following Table 1:

[Table 1]

	Bismuth acetate $(\text{CH}_3\text{CO}_2)_3\text{Bi}$, ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	Iron nitrate $\text{Fe}(\text{NO}_3)_3$
	↘	↗
Step 1	Stirring for 1 hour	

Step 2	Setting of the pH with HNO_3
	Heating with microwaves to 150°C , for 10 min
	+ KOH and pH setting with NH_4OH
	Heating with microwaves to 200°C , for 30 min
	Centrifugation and washing

Example 2: Synthesis of a catalytic system of the invention through a microwave-assisted hydrothermal reaction

The industrial catalysts currently contain several typical phases MoO_3 , $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, $\text{Fe}_2(\text{MoO}_4)_3$, $\text{Fe}_x\text{Co}_{1-x}\text{MoO}_4$, NiMoO_4 , $\text{Bi}_2\text{Mo}_2\text{O}_9$...

The two most useful phases are $\text{Fe}_x\text{Co}_{1-x}\text{MoO}_4$ and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. Since the iron/cobalt/molybdenum mixed phase is very difficult to synthesize through the precipitation/calcination method because of the oxidation of Iron II into Iron III, the synthesis of this phase on an industrial scale cannot be considered. Indeed, $\text{Fe}_2(\text{MoO}_4)_3$ is always formed.

It has been possible to synthesize the two phases according to a method of the invention involving a microwave-assisted hydrothermal synthesis, which allows getting rid of the oxidation of iron, through the following protocol:

$\text{Bi}_2\text{Mo}_3\text{O}_{12}$

Bismuth nitrate and nitric acid have been dissolved in 150 ml of bi-distilled water. A second solution has been prepared by dissolving the ammonium heptamolybdate in 100 mL of bi-distilled water. Afterwards, the two solutions have been mixed and the resulting mixture has been kept under stirring for 10 minutes at 300 rpm, the pH has been set to 1 by addition of ammonium hydroxide, it has been transferred afterwards into a 1 L Teflon vial for irradiation with microwaves.

The microwave-assisted hydrothermal synthesis has been performed at 150°C for 10 minutes. After treatment with microwaves, the collected product has been retrieved by centrifugation at 3000 rpm, and then washed twice with de-ionized water and ethanol. Finally, the sample has been dried at 90°C for 8 hours.

$\text{Fe}_x\text{Co}_{1-x}\text{MoO}_4$ with $0.5 < x < 0.9$

A first solution of sodium molybdate has been dissolved in 250 mL of bi-distilled H_2O . Afterwards, iron II chloride and cobalt nitrate hexahydrate have been dissolved in 250 ml of triethylene glycol. Afterwards, the two solutions have been mixed and the resulting solution has been kept under stirring for 10 minutes at 300 rpm. Then, the solution is transferred into a 1 L Teflon vial for irradiation with microwaves. The microwave-assisted hydrothermal synthesis has been carried out at 150°C for 10 min. After treatment with microwaves, the collected product has been

retrieved by centrifugation at 3000 rpm, then washed twice with water and ethanol. Finally, the sample has been dried at 90°C for 8 hours.

Example 3:

In this example, the catalyst prepared by microwaves has been tested in the controlled oxidation reaction of propene into acrolein and compared at iso-mass with the industrial catalyst prepared by calcination. The stoichiometry of the catalyst is: $\text{Mo}_{12}\text{Co}_{7.12}\text{Fe}_{1.8}\text{Bi}_{0.65}\text{K}_x$.

The test is done under a gas stream constituted by $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2$: 1/1.5/8.6, for a total gas flow rate of 60 ml/min with 250 mg of catalyst and at 350°C. Table 2 hereinbelow provides the propene conversion and the acrolein selectivity after 48h under a gas stream.

[Table 2]

	Industrial catalyst	Microwaves catalyst
Propene conversion	11 %	34 %
Acrolein selectivity	94 %	92 %

Example 4

In this example, catalysts prepared by microwaves and having different stoichiometries in Mo have been compared to one another in the controlled oxidation reaction of propene into acrolein.

The test is done under a gas stream constituted by $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2$: 1/1.5/8.6, for a total gas flow rate of 60 ml/min with 250 mg of catalyst and at 350°C. Table 3 hereinbelow provides the propene conversion and the acrolein selectivity after 48h under a gas stream.

[Table 3]

	$\text{Mo}_8\text{Co}_{7.12}\text{Fe}_{1.8}\text{Bi}_{0.65}\text{K}_x$	$\text{Mo}_{10}\text{Co}_{7.12}\text{Fe}_{1.8}\text{Bi}_{0.65}\text{K}_x$	$\text{Mo}_{12}\text{Co}_{7.12}\text{Fe}_{1.8}\text{Bi}_{0.65}\text{K}_x$
Propene conversion	2 %	5 %	34 %
Acrolein selectivity	69%	95 %	92 %

Example 5

In this example, catalysts prepared by microwaves and having different stoichiometries in Bi have been compared to one another in the controlled oxidation reaction of propene into acrolein.

The test is done under a gas stream constituted by $C_3H_6/O_2/N_2$: 1/1.5/8.6, for a total gas flow rate of 60 ml/min with 250 mg of catalyst and at 350°C. Table 4 hereinbelow provides the propene conversion and the acrolein selectivity after 48h under a gas stream.

[Table 4]

	Mo₁₂Co_{7.12}Fe_{1.8}Bi_{0.65}K_x	Mo₁₂Co_{7.12}Fe_{1.8}Bi_{0.5}K_x	Mo₁₂Co_{7.12}Fe_{1.8}Bi_{0.2}K_x
Propene conversion	34 %	10 %	11 %
Acrolein selectivity	92 %	93 %	94 %

Example 6

In this example, the catalyst prepared by microwaves has been tested in the controlled oxidation reaction of propene into acrolein. The stoichiometry of the catalyst MW is: Mo₁₂Co_{7.12}Fe_{1.8}Bi_{0.65}K_x.

The test is done under a gas stream constituted by $C_3H_6/O_2/N_2$: 1/1.5/8.6, for a total gas flow rate of 60 ml/min with 250 mg of catalyst and at 350°C. Table 5 hereinbelow provides the propene conversion and the acrolein selectivity after 358h under a gas stream.

[Table 5]

	Microwaves catalyst
Propene conversion	22 %
Acrolein selectivity	96 %

Example 7

In this example, the catalyst prepared by microwaves with nickel has been tested in the controlled oxidation reaction of propene into acrolein. The stoichiometry of this catalyst is: Mo₁₂Co₄Ni_{3.12}Fe_{1.8}Bi_{0.65}K_x.

The test is done under a gas stream constituted by $C_3H_6/O_2/N_2$: 1/1.5/8.6, for a total gas flow rate of 60 ml/min with 250 mg of catalyst and at 350°C. Table 6

hereinbelow provides the propene conversion and the acrolein selectivity after 48h under a gas stream.

5

[Table 6]

	Catalyst Mo₁₂Co₄Ni_{3,12}Fe_{1,8}Bi_{0,65}K_x.
Propene conversion	11 %
Acrolein selectivity	92 %

Example 8

In this example, the catalyst prepared by microwaves is prepared by mechanical mixtures of the useful phases: Fe_xCo_{1-x}MoO₄ and Bi₂Mo₃O₁₂.

10

[Table 7]

weight% Fe_{0.67}Co_{0.33}MoO₄*	weight% Bi₂Mo₃O₁₂	Propene conversion (%)	Acrolein selectivity (%)
100	0	2 ± 1 %	21 ± 2 %
90	10	68 ± 1 %	77 ± 2 %
80	20	70 ± 1 %	73 ± 2 %
70	30	73 ± 1 %	76 ± 2 %
60	40	70 ± 1 %	74 ± 2 %
0	100	6 ± 1 %	74 ± 2 %

* Fe_xCo_{1-x}MoO₄ with x = 0.67

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The test is done under a gas stream constituted by C₃H₆/O₂/N₂: 1/1.5/8.6, for a total gas flow rate of 60 ml/min with 250 mg of catalyst and at 350°C. Table 7 hereinbelow provides the propene conversion and the acrolein selectivity after 48h under a gas stream.

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CLAIMS

[Claim 1] A method for producing a multiphase mixed-oxide catalyst comprising at least one active phase based on bismuth molybdate and one co-catalyst based on iron molybdate and at least one amongst the two elements cobalt and nickel, said method being characterized in that it comprises the following steps:

- preparing a mixture of the precursors of said mixed oxides in a solvent,
- making said precursors react through a microwave-assisted hydrothermal reaction, and
- isolating the mixed oxides to obtain the catalyst.

[Claim 2] The production method according to claim 1, characterized in that said precursors are reacted through a microwave-assisted hydrothermal reaction in two steps, a first microwave-assisted hydrothermal reaction and a second microwave-assisted hydrothermal reaction, between which the pH of the reaction mixture obtained from the first microwave-assisted hydrothermal reaction is set to 8-8.5.

[Claim 3] The production method according to claim 1 or 2, characterized in that the catalyst comprises molybdenum oxide.

[Claim 4] The production method according to any one of claims 1 to 3, characterized in that the catalyst is supported, said method comprising the addition of one or several support material(s), before the microwave-assisted hydrothermal reaction(s).

[Claim 5] The production method according to any one of claims 1 to 4, characterized in that the microwave-assisted hydrothermal reaction(s) is/are performed at a temperature from 150°C to 240°C.

[Claim 6] The production method according to any one of claims 1 to 5, characterized in that the microwave-assisted hydrothermal reaction(s) is/are carried out over a time period from 2 minutes to 10 hours.

[Claim 7] The production method according to any one of claims 1 to 6, characterized in that the active phase of the catalyst meets the following stoichiometry $\text{Bi}_x\text{Mo}_y\text{O}_z$ where $2 > x/y > 0.5$ and z is comprised between 6 and 12; preferably this stoichiometry is selected amongst $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, $\text{Bi}_2\text{Mo}_2\text{O}_9$ and Bi_2MoO_6 .

[Claim 8] The production method according to any one of claims 1 to 7, characterized in that the active phase of the catalyst is activated by at least one alkali metal, preferably at least potassium.

5

[Claim 9] The production method according to any one of claims 1 to 8, characterized in that the co-catalyst meets the following stoichiometry $\text{Fe}_x\text{Co}_{1-x}\text{MoO}_4$ where x is a decimal number such that $0 < x < 1$, preferably such that $0.5 \leq x \leq 0.9$.

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[Claim 10] The production method according to any one of claims 1 to 9, characterized in that the catalyst meets the formula $\text{Mo}_m\text{Co}_n\text{Ni}_p\text{Fe}_q\text{Bi}_r\text{M}_s$ where M is an alkali metal, m , n , p , q , r and s are natural or decimal numbers, with m varying from 1 to 5, n and p varying independently of one another from 0 to 1 with $n+p$ different from 0, $0 < q \leq 1$, $0 < r \leq 3$ and $0 < s \leq 0.2$.

15

[Claim 11] The production method according to any one of claims 1 to 10, characterized in that:

- a mixture of the precursors of the active phase in a solvent, on the one hand, and a mixture of the precursors of the co-catalyst in the same solvent or in another solvent, on the other hand, are prepared;
- the precursors of the active phase and the precursors of the co-catalyst are reacted separately, through a microwave-assisted hydrothermal reaction;
- the active phase and the co-catalyst, respectively, are isolated; and
- the active phase and the co-catalyst are assembled to obtain the catalyst.

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[Claim 12] The production method according to any one of claims 1 to 11, characterized in that the mixture(s) of the precursors of the mixed oxides is/are obtained in one or more of the solvents selected from water, organic solvents and any combination of said organic solvents together or with water.

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[Claim 13] The production method according to claim 11 or 12, characterized in that the catalyst is supported, said method comprising the addition of one or several support material(s), and/or the catalyst comprises molybdenum oxide, said method comprising the addition of molybdenum oxide, the addition of said support material(s) and/or of the molybdenum oxide being carried out during the synthesis or the assembly of the active phase and of the co-catalyst to obtain the catalyst.

35

[Claim 14] The production method according to any one of claims 1 to 13, for the production of a multiphase mixed-oxide catalyst intended for at least one amongst the following catalytic reactions: the oxidation of propene into acrolein, the oxidative dehydrogenation of butene into butadiene, the oxidation of isobutylene into methacrolein, the ammoxidation of propene into acrylonitrile and the ammoxidation of isobutylene into methacrylonitrile.

[Claim 15] A catalytic system comprising separately at least one active phase based on bismuth molybdate and one co-catalyst based on iron molybdate and at least one amongst cobalt and nickel.

[Claim 16] The catalytic system according to claim 15, characterized in that the active phase meets the following stoichiometry $\text{Bi}_x\text{Mo}_y\text{O}_z$ where $2 > x/y > 0.5$ and z is comprised between 6 and 12; preferably this stoichiometry is selected amongst $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, $\text{Bi}_2\text{Mo}_2\text{O}_9$ and Bi_2MoO_6 .

[Claim 17] The catalytic system according to claim 15 or 16, characterized in that the active phase is activated by at least one alkali metal, preferably at least potassium.

[Claim 18] The catalytic system according to any one of claims 15 to 16, characterized in that the co-catalyst meets the following stoichiometry $\text{Fe}_x\text{Co}_{1-x}\text{MoO}_4$ where x is a decimal number such that $0 < x < 1$, preferably such that $0.5 \leq x \leq 0.9$.

[Claim 19] The catalytic system according to any one of claims 15 to 18, characterized in that the active phase content is lower than or equal to 50 weight% with respect to the weight of the catalytic system, preferably it varies from 10% to 45%.

[Claim 20] A use of a catalytic system according to any one of claims 15 to 19, for at least one amongst the following catalytic reactions: the oxidation of propene into acrolein, the oxidative dehydrogenation of butene into butadiene, the oxidation of isobutylene into methacrolein, the ammoxidation of propene into acrylonitrile and the ammoxidation of isobutylene into methacrylonitrile.