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 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 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 disclosure, in one aspect, concerns 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 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 reaction, and

isolating the mixed oxides to obtain the catalyst.

By microwaves according to the disclosure, 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 wavelengths are not authorized, preference will be given, yet without the disclosure 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.

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 disclosure, said precursors are reacted through a microwave-assisted hydrothermal reaction in two steps, namely: 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.

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 microwaves 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 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 disclosure has the following features, which may be considered separately or in any combination:

it further comprises molybdenum oxide;

it is supported; in the method of the disclosure, 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 disclosure may be supported afterwards according to any technique well known to those skilled in the art;

the active phase of the catalyst meets the following stoichiometry $Bi_xMo_yO_z$ where $2 > x/y > 0.5$ and z is comprised between 6 and 12; still preferably this stoichiometry is selected amongst $Bi_2Mo_3O_{12}$, $Bi_2Mo_2O_9$ and Bi_2MoO_6;

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 $Fe_xCo_{1-x}MoO_4$ 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 $Mo_mCo_nNi_pFe_qBi_rM_s$ 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 $0 < q \leq 0.2$.

The disclosure also concerns the catalyst obtained in this manner.

In a particular implementation of the method of the disclosure:

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.

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 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 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. 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 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, 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 disclosure, in another aspect, concerns 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. 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 $Bi_xMo_yO_z$ where $2 > x/y > 0.5$ and z is comprised between 6 and 12; preferably this stoichiometry is selected amongst the following ones: $Bi_2Mo_3O_{12}$, $Bi_2Mo_2O_9$ 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 $Fe_xCo_{1-x}MoO_4$ 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 disclosure, in another aspect, 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 $(NH_4)_6Mo_7O_{24}$ 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, $Bi_5O(OH)_9(NO_3)_4$, and in order to promote the complete dissolution of bismuth with 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