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(54) Title: METHOD FOR THE CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS

(57) Abstract: A catalyst for the full oxidation of volatile organic compounds (VOC), particularly hydrocarbons, and of CO to CO_2, comprising: a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $A_{14}Cu_{24}O_{41}$ (I), where A is Sr or a solid solution of Sr with alkaline-earth metals, alkaline metals, lanthanides; or a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $B_4Cu_5O_{10}$ (II), where B is Ca or a solid solution of Ca with alkaline-earth metals, alkaline metals, lanthanides; or mixtures thereof; and in that it is prepared in a form which has a large specific surface area, preferably larger than 25 m^2/g; a method for preparing the catalysts; their use in methods for the full oxidation of VOC and of CO to CO_2; and the oxidation methods.

METHOD FOR THE CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS

Technical Field

The present invention relates to catalysts for the full oxidation of volatile organic compounds (VOC), particularly hydrocarbons, and to a method for the full oxidation of volatile organic compounds (VOC) by using said catalysts.

Background Art

The total combustion of VOC to CO_2 and H_2O becomes necessary in view of the toxicity and environmental impact of most unburnt VOC. The goal is to minimize the release of VOC into the atmosphere and the forming of CO, which is in turn a toxic component.

The catalysts used most for VOC combustion are:

a) catalysts based on noble metals, which are characterized by a high cost but also by excellent performance in terms of VOC conversion, and operate at temperatures from 200 to 450°C according to the reactivity of the compound;

b) catalysts based on mixed oxides, typically chromites of copper or of other metals, or barium hexaaluminate, which are characterized by a lower cost but are active in more drastic conditions (temperatures from 400 to 600°C). This second class of catalysts is also used for catalytic combustors for power generation units. In this case, they operate at temperatures above 900°C.

The types of catalyst used for the combustion of VOC are not free from drawbacks; high cost (for those based on noble metals) and poor activity (for the second class, accordingly requiring operation at higher temperatures, in conditions in which morphologic or structural transformations are facilitated).

Disclosure of the Invention

The aim of the present invention is to eliminate the drawbacks of known types of catalyst for the full oxidation of VOC.

In particular, an object of the present invention is to provide catalysts for catalytic combustion which are characterized by high activity, high resistance to temperature, extreme operating conditions, low cost and easy production even as composites and thin films.

Another object of the present invention is to provide catalysts for VOC oxidation with high selectivity for carbon dioxide CO_2 with respect to carbon monoxide CO.

Another object of the present invention is to provide catalysts which lead to full oxidation of the VOC in stoichiometric and non-stoichiometric mixtures of VOC and oxygen (oxidizing or reducing conditions), so that the mixture of gases produced due to VOC oxidation contains no carbon monoxide but contains only carbon dioxide.

Another object of the present invention is to provide a method for the full oxidation of VOC which avoids carbon monoxide removal operations and the known negative consequences of the presence of carbon monoxide in the environment.

Another object is to provide a method for oxidizing VOC to CO_2 which utilizes the full potential of the VOC oxidation reaction, with evident energy-related advantages.

Another object is to provide a method for eliminating carbon monoxide from gas mixtures that contain it together with oxygen.

Ways of carrying out the Invention

This aim, these objects and others which will become apparent from the detailed description of the invention are achieved by catalysts according to the present invention, which comprise one or more non-stoichiometric crystalline compounds conventionally referenced by formulas which respectively correspond to:

1) $A_{14}Cu_{24}O_{41}$.

2) $B_4Cu_5O_{10}$ ($BCuO_2$ is also cited in the literature)

and by a method for oxidizing VOC and CO to CO_2 according to the present invention, which uses the same catalysts.

In the first of the above cited formulas, A is Sr or a solid solution of Sr with alkaline-earth metals, alkaline metals, lanthanides; in the second formula, B is Ca or a solid solution of Ca with alkaline-earth metals, alkaline metals, or lanthanides.

Examples of catalysts according to the invention have the approximate formula

$$Sr_{14}Cu_{24}O_{41}$$

or

$$Ca_4Cu_5O_{10}$$

Both of these compounds and their derivatives by substitution are widely known in the literature (for $Ca_4Cu_5O_{10}$ (mentioned as $CaCuO_2$): Roth et al, J Am Ceram Soc, Vol. 72, p. 1545 (1989); for $Sr_{14}Cu_{24}O_{41}$: McCarron et al, Mat Res Bull, Vol. 23, p. 1355 (1988)), and particularly for the compound $Sr_{14}Cu_{24}O_{41}$ there is a vast body of literature associated with its unusual electronic properties. Although it is not possible to formulate exactly the above components, they are unequivocally distinguished by their chemical-physical properties and particularly by the powder diffraction profiles, which correspond to the ones listed in JCPDS international powder diffraction tables, on cards 43-0025 and 46-0054 for the compounds referred to as $Sr_{14}Cu_{24}O_{41}$ and $CaCuO_2$, respectively.

The fixing properties of said compounds and derivatives thereof have been described in patent application BO98A000593 herein incorporated by reference. The same patent application describes the use of said compounds to fix gases and gas fixing devices which comprise said compounds.

The inventors have now found that surprisingly said compounds, if prepared so as to have a large specific surface area, preferably larger than $25m^2/g$ (as measured by the BET method), act as catalysts for VOC oxidation. The inventors have found that the reaction for full oxidation of

VOC in the presence of the catalysts according to the invention occurs with a high conversion of VOC even at low temperatures.

Moreover, the inventors have found that the catalysts according to the present invention allow VOC oxidation (even when the conversion is partial) with total selectivity toward the forming of CO_2 even in conditions in which there is a significant deficit of oxygen with respect to the stoichiometric mix. The expression “total selectivity” is used to reference the fact that VOC oxidation occurs until only CO_2 and H_2O are obtained. In other words, in conditions of oxygen deficit, while the quantity that corresponds stoichiometrically to the quantity of oxygen that is present is converted into CO_2 and H_2O, the other fraction of VOC remains unconverted.

The temperature ranges over which the catalytic oxidation process is active depend crucially on the volatile organic compound to be oxidized. Considering methane as the most stable and least easily oxidizable hydrocarbon, the activation temperatures of the reaction for full oxidation of methane constitute the upper limit of the activation temperatures for any VOC: in particular, the activation temperatures of methane are from 300°C to 350°C and from 350°C to 400°C for the compounds $A_{14}Cu_{24}O_{41}$ and $B_4Cu_5O_{10}$, respectively. The maximum utilization temperatures of the catalysts instead correspond to the decomposition temperatures of the compounds $A_{14}Cu_{24}O_{41}$ and $B_4Cu_5O_{10}$, which are proximate to 1000°C and 750°C, respectively.

The methods for full oxidation of VOC according to the present invention may be performed in combustion chambers or in reheat chambers or flue gas chambers.

The catalytic oxidation reaction of the catalysts according to the present invention occurs on a fixed bed or on a fluid bed.

The catalysts according to the present invention can be in the form of granules.

Advantageously, the catalysts according to the present invention include a substrate material. The substrate can be an inert substrate in the form of a thin film or a composite material. Preferably, the substrate material is constituted by porous substrates which are inert with respect to the above described active materials, such as Al_2O_3, TiO_2, ZrO_2, CeO_2, MgO, on which the active material is deposited by impregnation with the aqueous solution of soluble salts (for example nitrates or citrates or acetates or mixtures thereof) of the constituent metals in the correct stoichiometric ratios.

The catalysts according to the invention preferably comprise 5 to 20% by weight of a non-stoichiometric crystalline compound, conventionally designated by a formula which corresponds to $A_{14}Cu_{24}O_{41}$ (I), where A is Sr or a solid solution of Sr with alkaline-earth metals, alkaline metals, lanthanides; or a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $A_4Cu_5O_{10}$ (II), where A is Ca or a solid solution of Ca with alkaline-earth metals, alkaline metals, lanthanides; or mixtures thereof.

A catalyst comprising a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $Sr_{14}Cu_{24}O_{41}$ can be prepared, for example, with a method according to the invention which comprises the steps of:

a) immersing a pre-dried granular porous substrate material in an aqueous solution with a molar concentration of $Sr(NO_3)_2$ from 0.23 M to 0.93 M and a molar concentration of $Cu(NO_3)_2$ from 0.39 M to 1.59 M;

b) drying at a temperature from 80°C to 120°C;

c) holding at a temperature from 650°C to 750°C in a gas stream which contains oxygen until complete decomposition of the nitrates occurs.

A catalyst comprising a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $Ca_4Cu_5O_{10}$ is prepared with a method according to the invention which comprises the steps of:

a) immersing a pre-dried granular porous substrate material in an aqueous solution of $Ca(NO_3)_2$ and $Cu(NO_3)_2$ in an equimolar ratio and at a molar concentration from 0.39 M to 1.39 M;

b) drying at a temperature from 80°C to 120°C;

c) holding at a temperature from 650°C to 750°C in a gas stream which contains oxygen until complete decomposition of the nitrates occurs.

Furthermore, a catalyst comprising a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $Ca_4Cu_5O_{10}$ is prepared with a method according to the invention which comprises the steps of:

a) immersing a pre-dried granular porous substrate material in an aqueous solution obtained by dissolving, with the application of heat, CuO and $CaCO_3$ in nitric acid, so that the molar ratio between the components of the solution is CuO : $CaCO_3$: HNO_3 = 1 : 0.83 : 3.2; water and citric acid is added thereto so that the citric acid : Cu molar ratio is from 3.5:1 to 4.0:1;

b) heating in air until combustion of the organic fraction of the absorbed material is achieved;

c) thermal treatment for 4 to 24 hours at a temperature from 650 to 750°C in a stream of gas containing oxygen.

Preferably, the porous material that is used is constituted by Al_2O_3, ZrO_2, CeO_2, TiO_2, MgO.

However, one should not consider the present invention to be limited to catalysts prepared with the described methods.

EXAMPLES

The catalysts according to the present invention and the oxidation method according to the present invention are described in greater detail hereinafter with examples which are given only by way of non-limitative illustration.

Examples of preparation

1) After drying at 150°C for 12 hours, an appropriate amount of porous

alumina with a particle size from 2 to 4 mm, specific surface area of approximately 400 m^2/cm^3 and capable of absorbing at least 1 ml of solution per gram is immersed in an aqueous solution of $Sr(NO_3)_2$ and of $Cu(NO_3)_2$, at a concentration of 0.556 M and 0.952 M, respectively. The amount of alumina used should be such as to absorb almost all the solution. The alumina impregnated by the solution is then dripped, dried at 80°C for 4 hours, and finally treated at 650°C in a stream of air or oxygen for 24 h. This method produces a catalyst which contains 12% by weight of $Sr_{14}Cu_{24}O_{41}$ compound and has a specific surface area in excess of 200 m^2/cm^3.

2) After drying at 150°C for 12 hours, an appropriate amount of porous alumina with a particle size from 2 to 4 mm, specific surface area of approximately 400 m^2/cm^3 and capable of absorbing at least 1 ml of solution per gram is immersed in an aqueous solution of $Ca(NO_3)_2$ and of $Cu(NO_3)_2$, in an equimolar ratio and at a concentration of 0.556 M. The amount of alumina used should be such as to absorb almost all the solution. The alumina impregnated by the solution is then dripped, dried at 80°C for 4 hours, and finally treated at 650°C in a stream of air or oxygen for 24 h. This method produces a catalyst which contains 7% by weight of $Ca_4Cu_5O_{10}$ compound and has a specific surface area in excess of 200 m^2/cm^3.

3) After drying at 150°C for 12 hours, an appropriate amount of porous alumina with a particle size from 40 to 80 mesh, specific surface area of approximately 400 m^2/cm^3 and capable of absorbing at least 1 ml of solution per gram is immersed in an aqueous solution obtained by dissolving, with the application of heat (80°C), one mole of CuO and 0.83 moles of $CaCO_3$ in nitric acid so that the nitric acid/copper oxide molar ratio is 3.2, water and citric acid being added thereto, in order to complete dissolution of the reagents, so that the citric acid/Cu molar ratio is 3.8. The amount of alumina used should be such as to absorb almost all the solution. The alumina impregnated by the solution is then dripped and heated in air until

combustion of the organic fraction of the absorbed material is achieved. The resulting material is then subjected to thermal treatment at 700°C in a stream of air or oxygen for 24 h. This method produces a catalyst which contains 11% by weight of $Ca_4Cu_5O_{10}$ compound and has a specific surface area in excess of 200 m^2/cm^3.

Example 1

$Sr_{14}Cu_{24}O_{41}$: Catalytic combustion of methane

A catalyst containing $Sr_{14}Cu_{24}O_{41}$ was used in catalytic methane combustion tests.

The catalyst was a composite material constituted by an inert porous substrate (Al_2O_3) containing 12% by weight of active compound (60 mg).

The tests were conducted in a quartz fixed-bed microreactor with a diameter of 4 mm, containing 500 mg of catalysts in granules with particle sizes from 20 to 30 mesh.

Methane and air were fed to the reactor so that the concentration of methane in the test was equal to 2% by volume. The tests were conducted at atmospheric pressure and at a spatial velocity, expressed as GHSV (gas hourly space velocity: hourly volumetric flow-rate in feed/volume or weight of catalyst), equal to 80,000 cm^3/gh and 55,000 cm^3/gh, respectively. The mixture of the reaction products was analyzed by gas chromatography. The only products formed during the tests were carbon dioxide and water.

The results of the tests at various spatial velocities were found to be identical within the experimental error: the result obtained at 80,000 cm^3/gh is plotted in Figure 1, where the term "conversion" references the percentage in moles of converted methane with respect to the moles of supplied methane. The expression "set temperature" designates the temperature of the mixture of gas fed to the reactor, and the term "measured temperature" designates the temperature of the gas mixture at the outlet of the reactor, which is considered equal to the temperature of the catalyst.

Methane conversion begins at a temperature from 300 to 350°C. The resulting conversion curve has an inflection point at the temperature of 500°C. Total conversion is achieved at 650°C. Throughout the conversion process, the only products obtained were CO_2 and H_2O.

From the point of view of molecule reactivity, methane is to be considered difficult to oxidize. The required reaction conditions are therefore extremely drastic if compared with the other paraffins, olefins or volatile organic compounds. The tests that have been conducted have shown that the compound according to the invention is capable of oxidizing methane at relatively low temperatures: this is an indicator of the high full oxidation capacity of the invention compounds. As regards the other volatile organic compounds, one should assume that total combustion occurs at markedly lower temperatures than those found for methane.

Example 2

$Ca_4Cu_5O_{10}$: Catalytic combustion of methane

A catalyst containing $Ca_4Cu_5O_{10}$ was used in catalytic methane combustion tests. The tests were conducted in a quartz fixed-bed microreactor with a diameter of 4 mm, containing 500 mg of catalysts in granules with particle sizes from 20 to 30 mesh.

The catalyst was a composite material constituted by an inert porous substrate (Al_2O_3) containing 7.5% by weight of active compound (38 mg).

Methane and air were fed to the reactor so that the concentration of methane in the test was equal to 2% by volume. The tests were conducted at atmospheric pressure and at a spatial velocity, expressed as GHSV (gas hourly space velocity: hourly volumetric flow-rate in feed/volume or weight of catalyst), equal to 80,000 cm^3/gh and 55,000 cm^3/gh, respectively. The mixture of the reaction products was analyzed by gas chromatography. The only products formed during the tests were carbon dioxide and water.

The results of the tests at various spatial velocities were found to be identical within the experimental error: the result obtained at 80,000 cm^3/gh is plotted in Figure 2, where the term “conversion” designates the percentage in moles of converted methane with respect to the moles of supplied methane. The expression “set temperature” designates the temperature of the mixture of gas fed to the reactor, and the term “measured temperature” designates the temperature of the gas mixture at the outlet of the reactor, which is considered equal to the temperature of the catalyst.

Methane conversion begins at a temperature from 350 to 400°C. The resulting conversion curve has an inflection point at the temperature of 550°C. Total conversion is achieved at 700°C. Throughout the conversion process, the only products obtained were CO_2 and H_2O.

Example 3

$Sr_{14}Cu_{24}O_{41}$: Tests of methane combustion in oxygen deficit conditions

A catalyst $Sr_{14}Cu_{24}O_{41}$, fully similar to the one used in the test cited in example 1, was used in tests of methane combustion in oxygen deficit conditions. The tests were conducted in a quartz fixed-bed microreactor with a diameter of 4 mm, which contained 200 mg of catalyst in granules whose dimensions were from 20 to 30 mesh. Methane, oxygen and helium in a proportion of 2:1:20 vol/vol were fed to the reactor. The test was conducted at atmospheric pressure and at a spatial velocity, expressed as GHSV, equal to 80,000 cm^3/gh. The mixture of the reaction products was analyzed by gas chromatography. The products present in the gases in output at temperatures below 900°C were carbon dioxide and water, generated in a stoichiometric quantity with respect to the fed oxygen and excess unreacted methane.

The results of the activity test are plotted in Figure 3, where the term “conversion” designates the percentage of moles of converted methane with respect to the moles of supplied methane. The amounts of methane and oxygen used in the experiment allow a maximum conversion of 25% of the methane. The maximum value achieved and plotted in Figure 3 is within the expected experimental error.

Example 4

$Ca_4Cu_5O_{10}$: Tests of methane combustion in oxygen deficit

A catalyst $Ca_4Cu_5O_{10}$, fully similar to the one used in the test cited in example 2, was used in tests of methane combustion in oxygen deficit conditions. The tests were conducted in a quartz fixed-bed microreactor with a diameter of 4 mm, which contained 500 mg of catalyst in granules whose dimensions were from 20 to 30 mesh. Methane, oxygen and helium in a proportion of 2:1:4 vol/vol/vol were fed to the reactor.

The test was conducted at atmospheric pressure and at a spatial velocity, expressed as GHSV, equal to 80,000 cm^3/gh. The mixture of the reaction products was analyzed by gas chromatography. The products present in the gases in output at temperatures below 720°C were carbon dioxide and water, generated in a stoichiometric quantity with respect to the fed oxygen and excess unreacted methane.

The results of the activity test are plotted in Figure 4, where the term "conversion" designates the percentage of moles of converted methane with respect to the moles of supplied methane. The amounts of methane and oxygen used in the experiment allow a maximum conversion of 25% of the methane. The maximum value achieved and plotted in Figure 4 is within the expected experimental error.

Example 5

$Sr_{14}Cu_{24}O_{41}$: Conversion of CO to CO_2

The catalyst $Sr_{14}Cu_{24}O_{41}$ prepared as described in example 1 was used in tests of conversion of carbon monoxide, CO, to carbon dioxide, CO_2. The tests were conducted in a quartz fixed-bed microreactor with a diameter of 4 mm, containing 0.5 g of catalyst in granules having dimensions from 20 to 30 mesh. Carbon monoxide, oxygen and nitrogen in a volumetric concentration of 1%, 5% and 94%, respectively, were fed to the reactor.

The test was conducted at atmospheric pressure and at a spatial velocity of 50,000 cm^3/hg. The mixture of reaction products was analyzed by gas chromatography, using helium as the carrier gas. The composition of the resulting mixture of gases was analyzed by measuring the concentrations of CO and CO_2, which were found to be consistent with the reaction $2CO + O_2 \Rightarrow 2CO_2$.

The results of the test are plotted in Figure 5, where the term "conversion" designates the percentage of moles of converted CO with respect to the moles of supplied CO.

Example 6

$Ca_4Cu_5O_{10}$: Conversion of CO to CO_2

A catalyst containing $Ca_4Cu_5O_{10}$ was used in tests of conversion of carbon monoxide, CO, to carbon dioxide, CO_2. The tests were conducted in a quartz fixed-bed microreactor with a diameter of 4 mm, containing 0.5 g of catalyst in granules having dimensions from 20 to 30 mesh. Carbon monoxide, oxygen and nitrogen in a volumetric concentration of 1%, 5% and 94%, respectively, were fed to the reactor.

The catalyst was a composite material constituted by an inert porous substrate (Al_2O_3) containing 11% by weight of active compound (55 mg).

The test was conducted at atmospheric pressure and at a spatial velocity of 50,000 cm^3/hg. The mixture of reaction products was analyzed by gas chromatography, using helium as the carrier gas. The composition of the resulting mixture of gases was analyzed by measuring the concentrations of CO and CO_2, which were found to be consistent with the reaction $2CO + O_2 \Rightarrow 2CO_2$.

The results of the test are plotted in Figure 6, where the term "conversion" designates the percentage of moles of converted CO with respect to the moles of supplied CO.

The catalysts according to the present invention and the method for full oxidation of VOC according to the present invention can be used with good results for organic compounds which are gaseous or vaporize at low temperature, achieving complete combustion at low temperature. The CO_2

selectivity of the catalysts according to the present invention is an important characteristic. Oxidation of VOC, particularly hydrocarbons, with catalysts which are not specific for combustion usually leads to the generation of both CO and CO_2. Both products are thermodynamically favored in the conditions that are normally used, and the ratio is therefore usually conditioned by kinetic factors.

Accordingly, the specificity of the catalyst in the forming of CO_2 is linked to the characteristics of the active centers. CO_2 is in fact the primary product, as demonstrated by the tests conducted by varying the contact time, which show that the conversion does not depend on the spatial velocity, and therefore does not derive from the intermediate forming of CO. It is also important to note that the primary carbon monoxide, i.e., the carbon monoxide that does not derive from partial oxidation of VOC, is converted efficiently into carbon dioxide at temperatures above 100°C in the case of $A_{14}Cu_{24}O_{41}$ and 150°C in the case of $Ca_4Cu_5O_{10}$ in the presence of oxygen at a concentration which is sufficient to allow the reaction.

The catalysts according to the present invention and the method for full oxidation of gaseous organic compounds can be used to reduce or eliminate many noxious components of combustion gases generated in any manner, for example from very large-scale electric power stations down to small combustors for home use, including the important applications in the field of engines and of vehicles with internal-combustion engines.

The selectivity of the CO_2 yield furthermore makes it particularly interesting to use the catalysts according to the present invention in burners for closed environments (gas stoves, water heaters for sanitary use, cooking equipment, et cetera), in which the presence of CO and in combustion products is notoriously a severe health hazard.

Furthermore, the catalysts according to the present invention, particularly the compounds of the $Sr_{14}Cu_{24}O_{41}$ type, convert the carbon monoxide that is present in gas mixtures containing oxygen into carbon dioxide in a very efficient way and at low temperature.

The catalysts for catalytic oxidation according to the present invention are characterized by high activity, comparable to that exhibited by the more expensive noble metals and by the material $Ba_2Cu_3O_6$, by high resistance to temperature and to extreme operating conditions, and by low cost and simple production even in the form of compounds and thin films.

Furthermore, like the material $Ba_2Cu_3O_6$, they have a selectivity for carbon dioxide, CO_2, with respect to carbon monoxide, CO. The advantages of the materials $A_{14}Cu_{24}O_{41}$ and $B_4Cu_5O_{10}$ with respect to the material $Ba_2Cu_3O_6$ relate to:

-- reduced limitation in the deposition of large quantities of active material of the supported catalyst containing Ca or Sr with respect to the catalyst containing Ba;

-- a very advantageous cost with respect to Ba compounds;

-- lack of toxicity of Ca and Sr with respect to heavy metals such as Ba;

-- exclusively for the compound $Sr_{14}Cu_{24}O_{41}$, higher catalytic activity in all full oxidation reactions for equal temperature conditions.

The catalysts according to the present invention lead to full oxidation of VOC in stoichiometric mixtures of methane and oxygen or in excess of oxygen (oxidizing conditions). In this manner, the mixture of gases produced by VOC oxidation contains no carbon monoxide but contains only carbon dioxide. In this manner, the operations for removing carbon monoxide, and the known negative consequences of its presence in the environment, are avoided. Moreover, by oxidizing the carbon monoxide to carbon dioxide, the entire potential of the VOC oxidation reaction is utilized, providing evident energy-related advantages.

The disclosures in Italian Patent Application No. BO99A000314 from which this application claims priority are incorporated herein by reference.

CLAIMS

1. A catalyst for the full oxidation of volatile organic compounds (VOC), particularly hydrocarbons, and of CO to CO_2, characterized in that it comprises:

a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $A_{14}Cu_{24}O_{41}$ (I), where A is Sr or a solid solution of Sr with alkaline-earth metals, alkaline metals, lanthanides; or a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $B_4Cu_5O_{10}$ (II), where B is Ca or a solid solution of Ca with alkaline-earth metals, alkaline metals, lanthanides; or mixtures thereof; and in that it is prepared in a form which has a large specific surface area, preferably larger than 25 m^2/g.

2. The catalyst according to claim 1, characterized in that it furthermore comprises a substrate material.

3. The catalyst according to claim 2, characterized in that the substrate material is a porous inert material.

4. The catalyst according to claim 3, characterized in that said porous inert substrate comprises a material chosen from the group constituted by Al_2O_3, ZrO_2, CeO_2, TiO_2, MgO.

5. The catalyst according to the preceding claims, characterized in that it is in form of granules.

6. The catalyst according to claim 2, characterized in that said substrate is an inert substrate in the form of a thin film.

7. The catalyst according to claim 2, characterized in that said substrate is a composite material.

8. The catalyst according to claim 1, characterized in that it comprises 5% to 20% by weight of a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $A_{14}Cu_{24}O_{41}$ (I), where A is Sr or a solid solution of Sr with alkaline-earth metals, alkaline metals, lanthanides; or a non-stoichiometric crystalline compound

conventionally designated by a formula which corresponds to $B_4Cu_5O_{10}$ (II), where B is Ca or a solid solution of Ca with alkaline-earth metals, alkaline metals, lanthanides; or mixtures thereof.

9. A method for full oxidation of volatile organic compounds (VOC), particularly hydrocarbons, characterized in that a catalyst according to claims 1 to 8 is used.

10. A method for converting carbon monoxide to carbon dioxide, characterized in that a catalyst according to claim 1 is used.

11. Use of a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $A_{14}Cu_{24}O_{41}$ (I), where A is Sr or a solid solution of Sr with alkaline-earth metals, alkaline metals, lanthanides; or a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $B_4Cu_5O_{10}$ (II), where B is Ca or a solid solution of Ca with alkaline-earth metals, alkaline metals, lanthanides; or mixtures thereof, to prepare a catalyst for full oxidation of VOC.

12. Use of a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $A_{14}Cu_{24}O_{41}$ (I), where A is Sr or a solid solution of Sr with alkaline-earth metals, alkaline metals, lanthanides; or a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $B_4Cu_5O_{10}$ (II), where B is Ca or a solid solution of Ca with alkaline-earth metals, alkaline metals, lanthanides; or mixtures thereof, to prepare a catalyst for converting carbon monoxide to carbon dioxide.

13. A method for preparing a catalyst comprising a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $Sr_{14}Cu_{24}O_{41}$, comprising the steps of:

a) immersing a pre-dried granular porous substrate material in an aqueous solution with a molar concentration of $Sr(NO_3)_2$ from 0.23 M to 0.93 M and a molar concentration of $Cu(NO_3)_2$ from 0.39 M to 1.59 M;

b) drying at a temperature from 80°C to 120°C;

c) holding at a temperature from 650°C to 750°C in a gas stream which contains oxygen until complete decomposition of the nitrates occurs.

14. A method for preparing a catalyst comprising a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $Ca_4Cu_5O_{10}$, comprising the steps of:

a) immersing a pre-dried granular porous substrate material in an aqueous solution of $Ca(NO_3)_2$ and $Cu(NO_3)_2$ in an equimolar ratio and at a molar concentration from 0.39 M to 1.39 M;

b) drying at a temperature from 80°C to 120°C;

c) holding at a temperature from 650°C to 750°C in a gas stream which contains oxygen until complete decomposition of the nitrates occurs.

15. A method for preparing a catalyst comprising a non-stoichiometric crystalline compound conventionally designated by a formula which corresponds to $Ca_4Cu_5O_{10}$, comprising the steps of:

a) immersing a pre-dried granular porous substrate material in an aqueous solution obtained by dissolving, with the application of heat, CuO and $CaCO_3$ in nitric acid, so that the molar ratio between the components of the solution is CuO : $CaCO_3$: HNO_3 = 1 : 0.83 : 3.2; water and citric acid being added thereto so that the citric acid : Cu molar ratio is from 3.5:1 to 4.0:1;

b) heating in air until combustion of the organic fraction of the absorbed material is achieved;

c) thermal treatment for 4 to 24 hours at a temperature from 650 to 750°C in a stream of gas containing oxygen.

16. The method according to claim 13, wherein the porous material is constituted by Al_2O_3, ZrO_2, CeO_2, TiO_2, MgO.

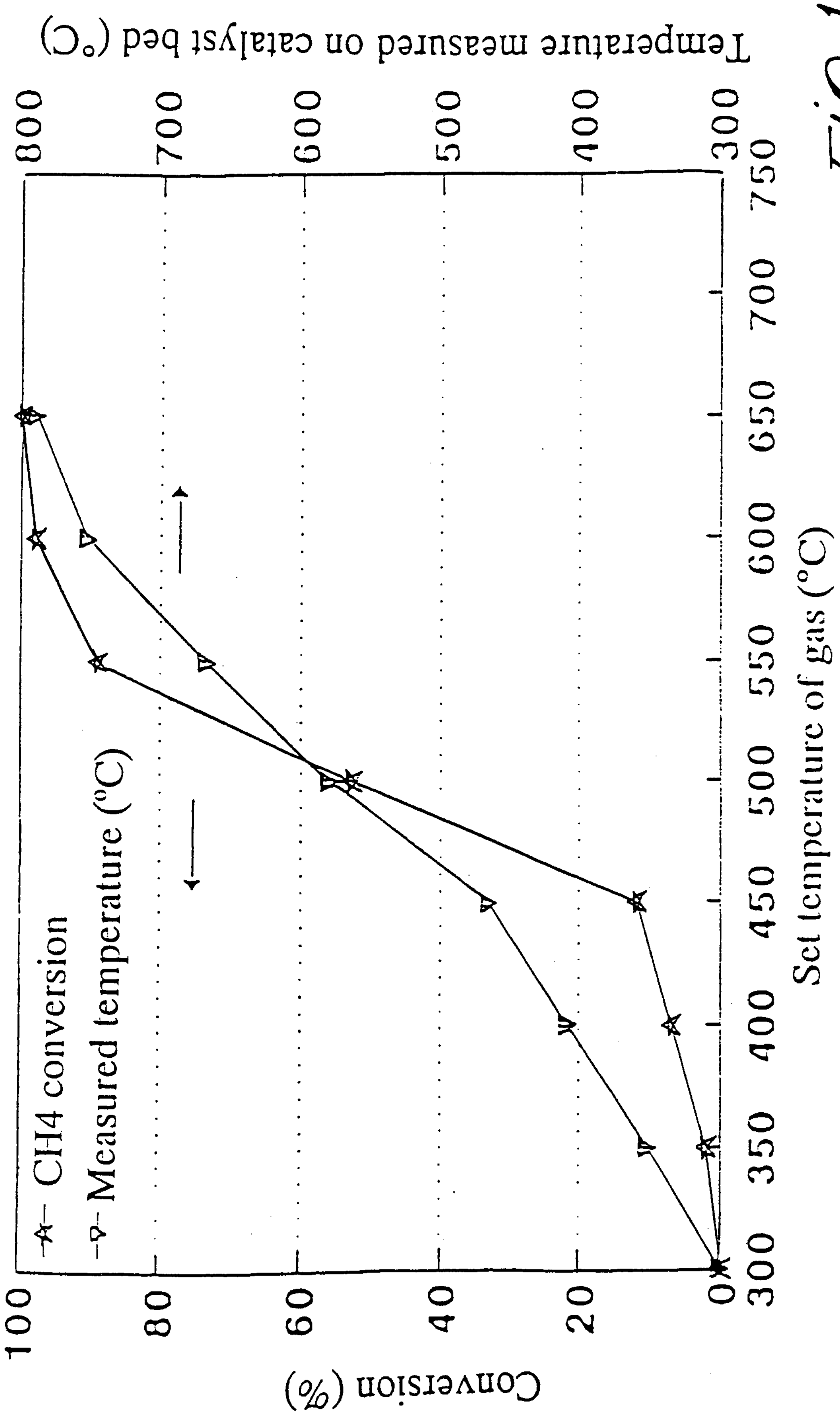

Fig. 1

Tests conducted with 0.5 g of catalyst by feeding with 700 ml/min air and 15 ml/min methane

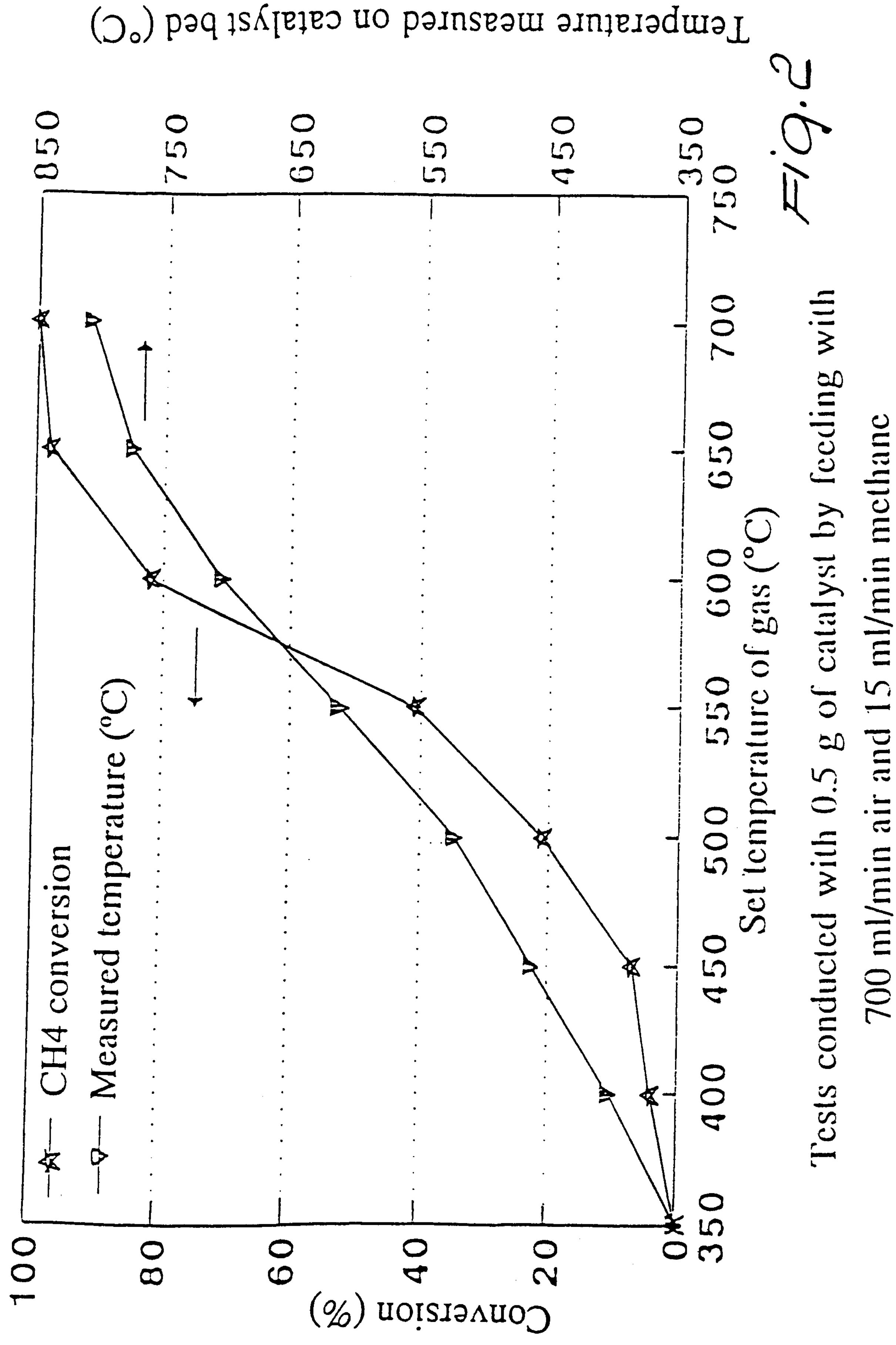
Temperature measured on catalyst bed (°C)
850
750
650
550
450
350
CH4 conversion
Measured temperature (°C)
Conversion (%)
100
80
60
40
20
0
350
400
450
500
550
600
650
700
750
Set temperature of gas (°C)
Tests conducted with 0.5 g of catalyst by feeding with
700 ml/min air and 15 ml/min methane

Fig.2

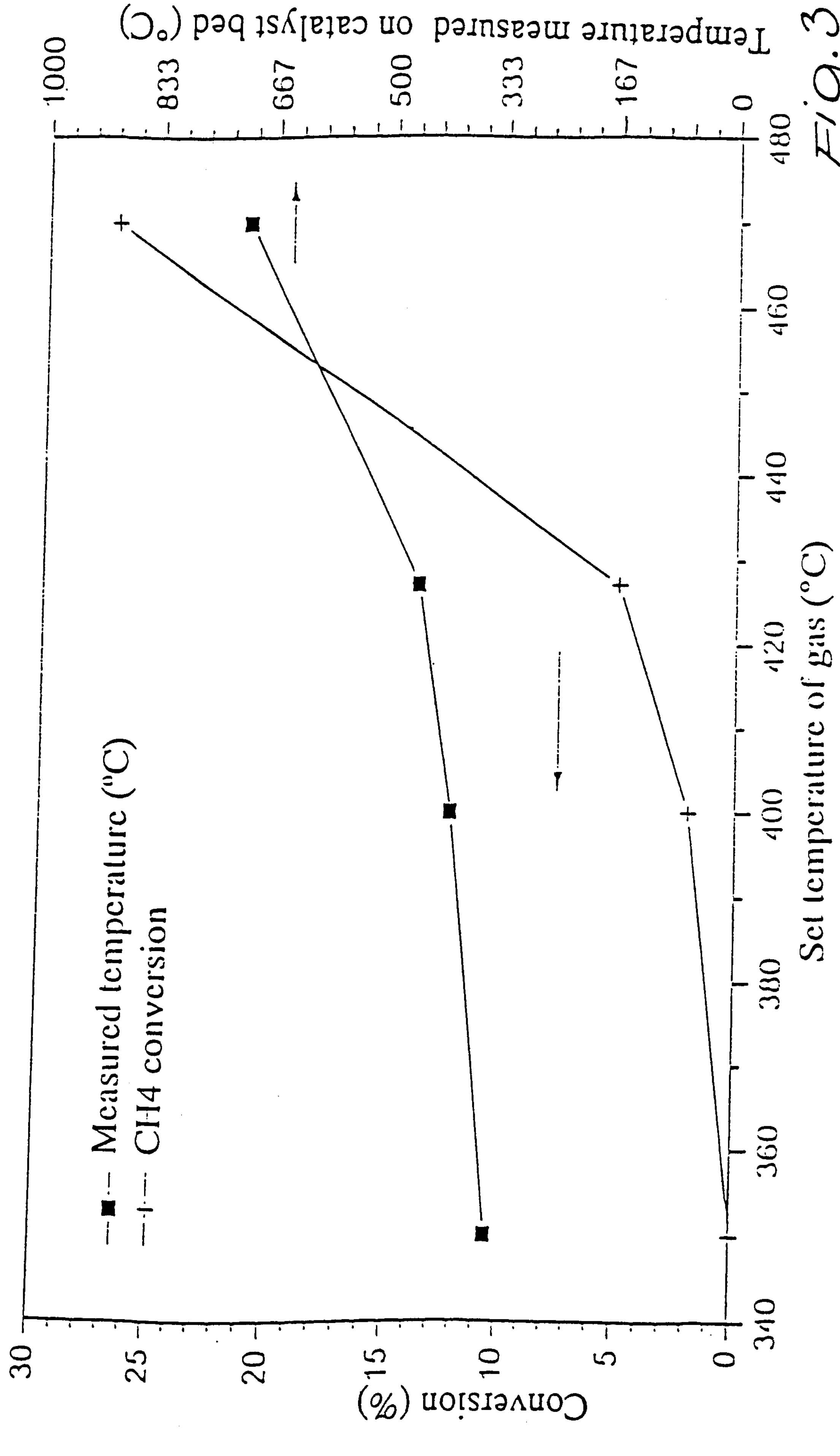

Fig. 3

Tests conducted with 0.2 g of catalyst by feeding with 60 ml/min methane, 30 ml/min oxygen, and 600 ml/min nitrogen

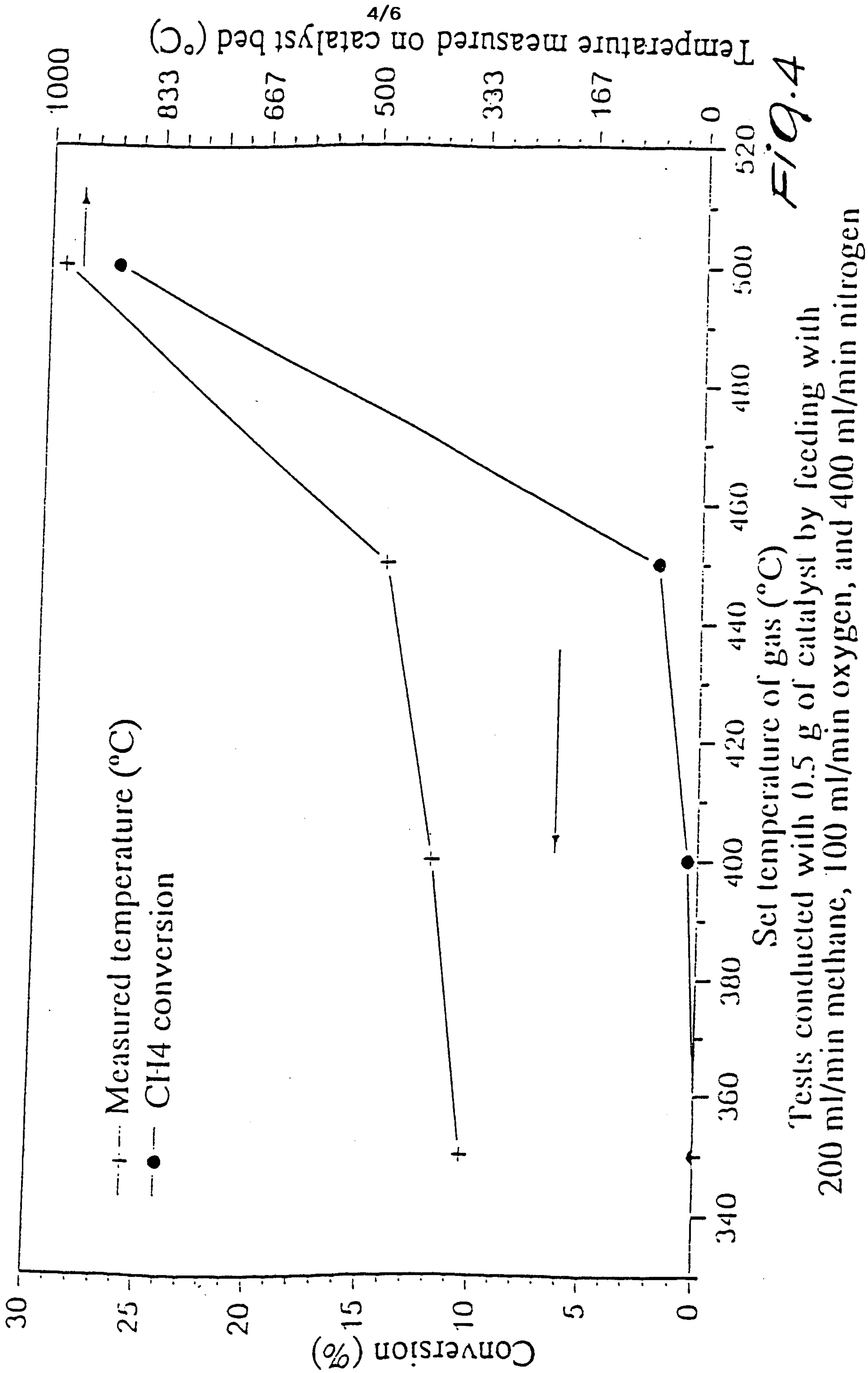
9/7
Temperature measured on catalyst bed (°C)
1000
833
667
500
333
167
0
Conversion (%)
30
25
20
15
10
5
0
340
360
380
400
420
440
460
480
500
520
Measured temperature (°C)
CH4 conversion
Set temperature of gas (°C)
Tests conducted with 0.5 g of catalyst by feeding with
200 ml/min methane, 100 ml/min oxygen, and 400 ml/min nitrogen

Fig.4

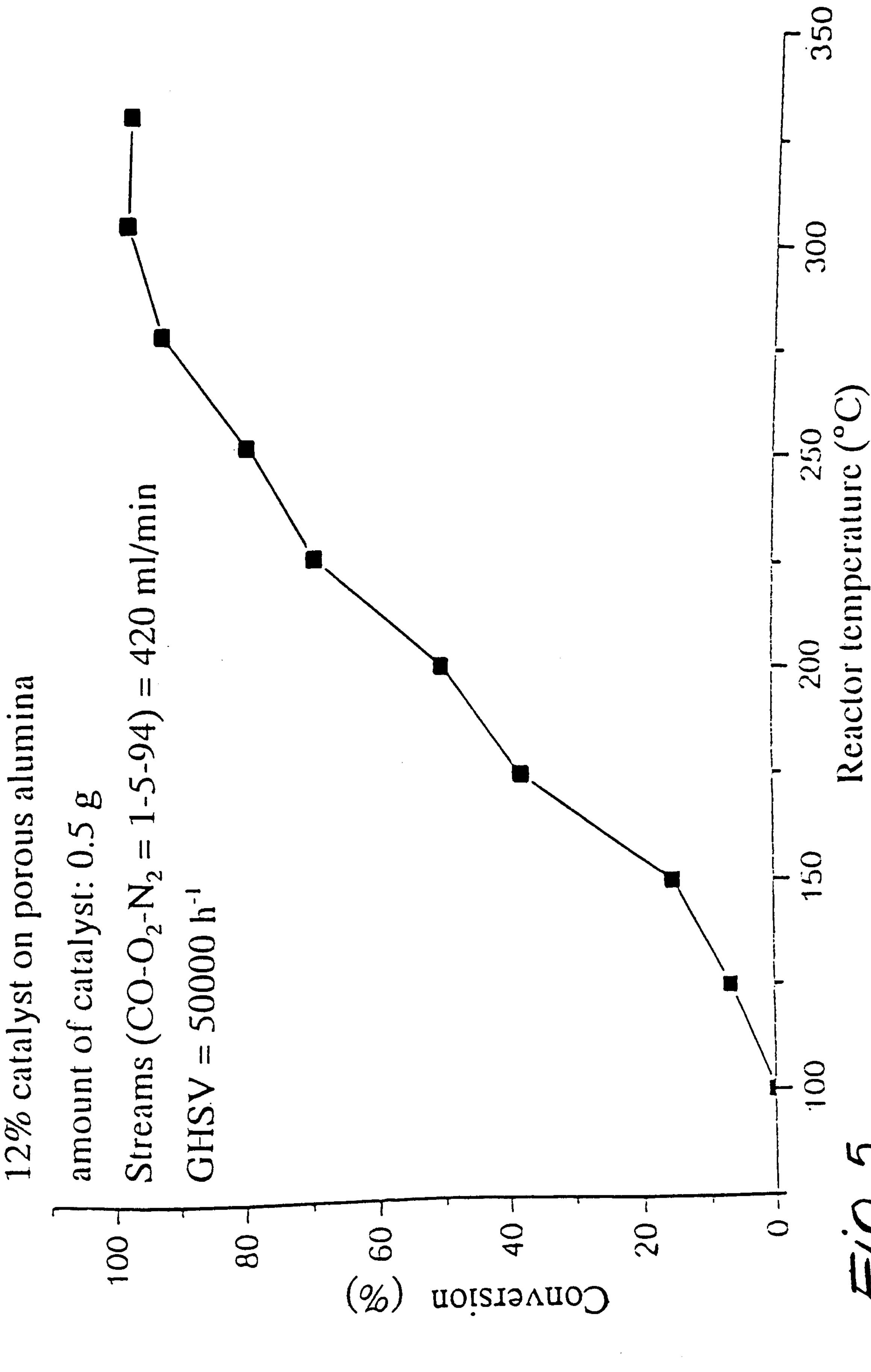
12% catalyst on porous alumina
amount of catalyst: 0.5 g
Streams (CO-O_2-N_2 = 1-5-94) = 420 ml/min
GHSV = 50000 h^{-1}
Conversion (%)
0
20
40
60
80
100
Reactor temperature (°C)
100
150
200
250
300
350

Fig. 5

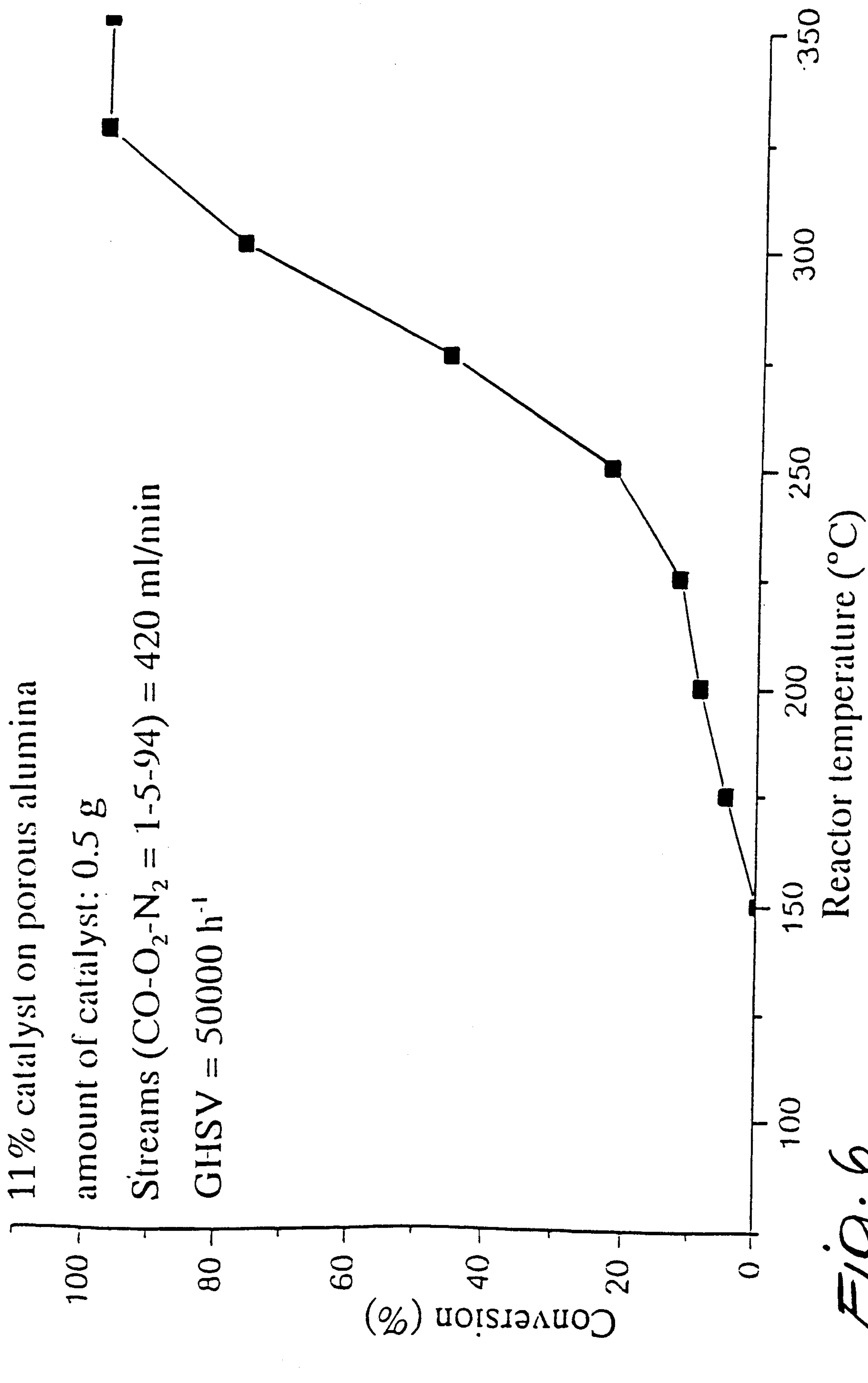
11 % catalyst on porous alumina
amount of catalyst: 0.5 g
Streams (CO-O2-N2 = 1-5-94) = 420 ml/min
GHSV = 50000 h-1
Conversion (%)
0
20
40
60
80
100
100
150
200
250
300
350
Reactor temperature (°C)

Fig. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/05196

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/86 B01J23/00 B01J23/28 B01J23/78

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 036 159 A (AUFDEMBRINK BRENT A ET AL) 30 July 1991 (1991-07-30) column 1, line 5 - line 20 column 1, line 28 - line 35 column 2, line 15 - line 19 ---	1-5,9-12
Y	DATABASE WPI Section Ch, Week 199540 Derwent Publications Ltd., London, GB; Class L03, AN 1995-308822 XP002149542 & JP 07 206436 A (TORAY IND INC), 8 August 1995 (1995-08-08) abstract --- -/--	1,9-12

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 October 2000	18/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Cubas Alcaraz, J

1

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 28887 A (MATACOTTA FRANCESCO C ;CAVANI FABRIZIO (IT); UNIV BOLOGNA (IT); CA) 14 August 1997 (1997-08-14) page 2, line 4 - line 24 page 3, line 18 -page 4, line 14 page 6, line 8 - line 17 page 8, line 10 - line 13	2-5
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A	MCCARRON ET AL.: "The incommensurate structure of (Sr14-xCax)Cu24041 (0<x<8) a superconductor byproduct" MAT. RES. BULL., vol. 23, 1988, pages 1355-1365, XP000946902 USA cited in the application page 1364	1

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Information on patent family members

Inte ional Application No
PCT/EP 00/05196

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SU 1641416	A	15-04-1991	NONE			