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(54) **MATERIAL FOR N<sub>2</sub>O DECOMPOSITION**

(57) The present invention concerns a material with a non-stoichiometric spinel-type crystalline structure based on cobalt oxide doped with alkaline elements, its production process for obtaining it by precipitation with controlled washing, and its particular use as a highly ac-

tive catalyst in the N<sub>2</sub>O decomposition reaction. Therefore, we understand that the present invention is in the area of green industry aimed at reducing N<sub>2</sub>O emissions into the atmosphere.

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**Description**

**[0001]** The present invention relates to a catalyst with a non-stoichiometric spinel-type crystalline structure, the production process for obtaining it via precipitation with controlled washing, and its particular use in the N<sub>2</sub>O decomposition reaction. Therefore, we understand that the present invention is in the area of green industry aimed at reducing N<sub>2</sub>O emissions.

**BACKGROUND TO THE INVENTION**

**[0002]** Nitrous oxide is a greenhouse gas with a potential 298 higher than CO<sub>2</sub> and with a devastating effect on the ozone layer, with a lifetime in the troposphere of 100 years. The industrial sector generates 5% of total N<sub>2</sub>O emissions and it is estimated that this is the sector that is likely to experience the largest increase in emissions in the very near future. Within the industrial sector, nitric acid and adipic acid production are the main sources of N<sub>2</sub>O emissions. Since the number of plants is limited, emission reductions could be easier to achieve compared to other sectors that have many diffuse sources, such as biomass burning or agriculture. Measures have already been established for a large number of the adipic acid plants, but emissions in nitric acid plants are particularly difficult to reduce.

**[0003]** The most effective technologies for nitrous oxide removal in nitric acid plants are catalytic decomposition processes carried out after the ammonia oxidation stage (secondary treatment) or its removal in the tail gas stream (tertiary treatment). There are several commercial catalysts available for secondary treatment, but they have some disadvantages, such as deactivation, low wear resistance or sintering of the active phase due to the high temperatures they have to withstand (between 750 °C and 940 °C).

**[0004]** The tertiary treatment offers the great advantage of not affecting the heart of the nitric acid plant since it is implemented as a tail gas treatment. The main technological problem is to develop catalytic systems that are active at relatively low temperatures (between 250 °C and 500 °C) and capable of operating under real process conditions, since there are other components present in the tail gas (O<sub>2</sub>, H<sub>2</sub>O and possibly NO<sub>x</sub>) that can significantly alter the efficiency of the catalyst.

**[0005]** Catalysts considered to be active in the decomposition reaction of N<sub>2</sub>O at low-temperature are zeolites modified with various metals (Cr, Mn, Fe, Co, Ni o Cu), noble metals (Rh, Ru, Pd) supported on ZnO, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> o ZrO<sub>2</sub>, hydrotalcite derivatives, spinels and metal oxides [M. Konsolakis, ACS Catal. 2015, 5, 6397-6421; J. Perez-Ramirez, Appl. Catal. B 44 (2003) 117-151]. Among them, those that have shown the best catalytic activities and the best resistance to O<sub>2</sub> and H<sub>2</sub>O are based on cobalt spinel. Yan et al [L. Yan, R. Ren, X. Wang, Q. Gao, D. Ji, J. Suo, Catal. Comm. 4 (2003) 505-509;

L. Yan, R. Ren, X. Wang, D. Ji, J. Suo, Appl. Catal. B 45 (2003) 85-90] published studies with the formulations Zn<sub>x</sub>Co<sub>1-x</sub>Co<sub>2</sub>O<sub>4</sub> and MxCo<sub>1-x</sub>Co<sub>2</sub>O<sub>4</sub> (M= Ni, Mg) where T<sub>50</sub> (temperature required for 50 % conversion of N<sub>2</sub>O) were recorded respectively at 250 and 220 °C. The operating conditions used were GHSV (gas hourly space velocity) of 15000 h<sup>-1</sup> and N<sub>2</sub>O concentrations of 1000 ppm, with 10% O<sub>2</sub> and 5% H<sub>2</sub>O. Similar results (T<sub>50</sub> = 260°C) were obtained by Xu et al. [L. Xue, C. Zhang, H. He, Y. Teraoka, Appl. Catal. B 75 (2007) 167-174] with its CoCe<sub>0.05</sub> catalyst also working at a space velocity of 15000 h<sup>-1</sup> and concentrations of 1000 ppm of N<sub>2</sub>O, 10% of O<sub>2</sub> and 3% of H<sub>2</sub>O.

**[0006]** The addition of alkaline elements enhances the catalytic activity of cobalt spinel Co<sub>3</sub>O<sub>4</sub> [JP2007054714 (A)]. Stelmachowski et al [P. Stelmachowski, G. Maniak, A. Kotarba, Z. Sojka, Catal. Comm. 10 (2009) 1062-1065] reported conversions of 50% at 335°C using K-doped cobalt spinels working at 7000 h<sup>-1</sup> and N<sub>2</sub>O concentrations of 1500 ppm and 1% de H<sub>2</sub>O, and Xue et al, 77% at 350°C [Li Xue, Changbin Zhang, Hong He, Yasutake Teraoka, Applied Catalysis B: Environmental, Volume 75, Issues 3-4, 2007, Pages 167-174]. In these studies, the presence of O<sub>2</sub> and H<sub>2</sub>O has been taken into account (even in higher concentrations than the actual ones), but the space velocities tested are nevertheless much lower than those used industrially. In addition, no stability tests were performed except in the case of the Co<sub>3</sub>O<sub>4</sub> catalyst promoted with K, where the catalyst was only evaluated for 10 h. Other authors have also described the behaviour of catalysts doped with other alkalis, such as Cs, with doping obtained by impregnation method. The addition of water in the feed, present in actual operating conditions, leads to a decrease in N<sub>2</sub>O conversion using these catalysts [Pawet Stelmachowski, Gabriela Maniak, Andrzej Kotarba, Zbigniew Sojka, Catalysis Communications, Volume 10, Issue 7, 2009, Pages 1062-1065].

**[0007]** Therefore, there is a need to provide catalysts that report more than 90% conversion at temperatures below 350°C under real conditions, and to provide catalysts that are stable under these conditions.

**DESCRIPTION OF THE INVENTION**

**[0008]** The present invention concerns a new material with the formula Co<sub>3</sub>O<sub>4-x/2</sub>A<sub>y</sub>, its preparation process and its use as a catalyst in the decomposition reaction of N<sub>2</sub>O.

**[0009]** In a first aspect the present invention relates to a material characterised in that it has a non-stoichiometric

spinel-type crystalline structure, the general formula of which is " $\text{Co}_3\text{O}_{4-x/2}\text{A}_y$ ", where "x" has a value of between 0.02 and 0.3, "A" is an alkaline element and "y" has a value of between 0.06 and 0.18, with an A/Co ratio of between 0.02 and 0.10; the primary particle size being equivalent to a crystallite size of between 5 and 30 nm.

**[0010]** In the present invention "non-stoichiometric spinel" is understood as any material having cubic structure of spinel-type cobalt oxide that is partially reduced, which generates oxygen vacancies, with the general formula  $\text{Co}_3\text{O}_{4-x/2}\text{A}_y$ , since there is a reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  induced by the presence of the alkali element.

**[0011]** The advantage associated with these catalysts is that they show surface desorption of oxygen at temperatures around  $100^\circ\text{C}$  and lattice desorption of oxygen at temperatures between 200 and  $300^\circ\text{C}$  because the  $\text{Co}^{2+}/\text{Co}^{3+}$  ratio in the catalyst is between 0.55 and 0.80.

**[0012]** The material is preferably mesoporous. In the present invention, "mesoporous material" means any material having pores with a predominant pore size between 2 nm and 50 nm.

**[0013]** The advantage of the material being mesoporous is the accessibility of gases to the catalytically active centres, based on an ideal ratio of pore volume to specific surface area. In a preferred embodiment, the material has a pore volume of between  $0.2\text{ cm}^3/\text{g}$  and  $0.4\text{ cm}^3/\text{g}$  and a specific surface area BET of between  $40\text{ m}^2/\text{g}$  and  $80\text{ m}^2/\text{g}$ , relatively high for a bulk material, resulting in a high gas-solid contact surface area which favours catalytic activity.

**[0014]** In another preferred embodiment, the alkali element A is K, x is 0.182, and y is 0.09

**[0015]** In another preferred embodiment the alkali element A is Cs, x is 0.235, and y is 0.15

**[0016]** Another aspect of the invention is a process for obtaining a  $\text{Co}_3\text{O}_{4-x/2}\text{A}_y$  material with a non-stoichiometric spinel structure characterised by the following steps:

- a) dissolving a cobalt salt in water;
- b) dissolving a salt or hydroxide of an alkali metal in water;
- c) slowly adding the solution obtained in step (b) to the solution prepared in step (a) until a pH of between 8 and 11 is reached;
- d) filtering the solid obtained in step (c) and washing it with 5 ml to 75 ml of water for each gram of cobalt salt added in step (a);
- e) drying the solid obtained in step (d) at a temperature between  $50^\circ\text{C}$  and  $200^\circ\text{C}$  for a time between 12 h and 20 h; and
- f) calcining the solid obtained in step (e) at a temperature between  $200^\circ\text{C}$  and  $700^\circ\text{C}$  in an air atmosphere for at least 30 min.

**[0017]** The washing in stage (d) is carried out in a controlled manner and is critical, since the content of A in the sample depends on it, and this directly influences the reduction temperature of Co(III) to Co(II) and, therefore, the  $\text{Co}^{2+}/\text{Co}^{3+}$  ratio obtained, thus controlling, depending on the amount of water used in relation to the initial Co salt content in the reaction, the amount of alkali to be introduced into the crystal lattice of the material of the present invention. Furthermore, this controlled washing avoids an additional stage in which the alkali metal is added, making the procedure of the present invention simpler than those described in the prior art.

**[0018]** According to the process described in the present invention, a non-stoichiometric cobalt spinel precipitation of cobalt oxide is produced, doped with an alkali metal in such a way that an intimate contact between the Co and the alkali ion is created from the stage of precipitate formation. The doping is of the bulk-type doping, with a distribution of the alkali element throughout the whole not just on the surface.

**[0019]** This synthesis process directly affects the cobalt spinel-formation process, generating a material with a primary particle size equivalent to the size of crystallite or crystalline domain, as revealed by X-ray diffraction and scanning electron microscopy. A small primary particle size of the cobalt spinel results in a high exposed specific surface area, leading to a high ratio of active centres per gram of catalyst, contributing to the improvement of catalyst efficiency.

**[0020]** In addition, the inclusion of the alkali ion by this process significantly alters the chemical-physical properties of the material, as it causes a partial reduction of Co(III) ions to Co(II). This changes the stoichiometry of the resulting spinel, decreasing the proportion of oxygen in the lattice, which leads to a distortion of the structure and gives it distinctly different catalytic properties than the conventional spinel.

**[0021]** In another preferred embodiment of the process, the cobalt salt in step (a) is selected from cobalt nitrate hexahydrate, cobalt sulphate, cobalt chloride and cobalt acetate.

**[0022]** In another preferred embodiment of the process the alkali metal salt or hydroxide of step (b) is selected from an alkali metal carbonate, alkali metal nitrate, alkali metal hydroxide and alkali metal acetate. In a more preferred embodiment, the alkali metal salt or hydroxide is alkali metal carbonate.

**[0023]** In another preferred embodiment of the process, if the cobalt salt is cobalt nitrate hexahydrate and the alkali metal salt is alkali metal carbonate, the washing of step (d) is with an amount of water between 16 ml/g and 21 ml/g of cobalt nitrate hexahydrate.

**[0024]** A third aspect of the present invention relates to the use of the material described above as a catalyst.

**[0025]** In a more preferred embodiment it refers to the use of the material as a catalyst in the oxidation/decomposition

of gases.

**[0026]** In a still more preferred embodiment it refers to the use of the material as a catalyst for N<sub>2</sub>O decomposition.

**[0027]** The catalysts show a N<sub>2</sub>O conversion of 98 % under real operating conditions from 340 °C at a GHSV of 50,330 h<sup>-1</sup>.

5 **[0028]** The catalysts show a N<sub>2</sub>O conversion of 98 % under real operating conditions from 310 °C at a GHSV of 24,000 h<sup>-1</sup>.

**[0029]** Furthermore, it shows a high stability in the presence of H<sub>2</sub>O and O<sub>2</sub> of at least 65 h without a decrease in the conversion of N<sub>2</sub>O and without altering determining properties such as particle size or porosity.

10 **[0030]** Throughout the description and claims the word "comprises" and its variants are not intended to exclude other technical features, additives, components or steps. Other objects, advantages and features of the invention will be apparent to those skilled in the art in part from the description and in part from the practice of the invention. The following examples and figures are provided by way of illustration, and are not intended to be limiting of the present invention.

## BRIEF DESCRIPTION OF THE FIGURES

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### **[0031]**

**Fig. 1** X-ray diffractograms of the materials of the invention.

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**Fig. 2** Scanning electron microscopy images of the materials of the invention.

**Fig. 3** Pore size distribution of the materials of the invention obtained by adsorption-desorption isotherms of N<sub>2</sub>.

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**Fig. 4** XPS diagrams of the materials of the invention.

**Fig. 5** Programmed temperature reduction with H<sub>2</sub> of the materials of the invention.

**Fig. 6** Desorption of O<sub>2</sub> at programmed temperature of the materials of the invention.

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**Fig. 7** Conversion of N<sub>2</sub>O as a function of space time in the presence of O<sub>2</sub> and H<sub>2</sub>O vapour of the materials of the invention and of materials reported in the state of the art.

## EXAMPLES

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**[0032]** The invention is illustrated below by means of the results of tests carried out by the inventors which demonstrate the effectiveness of the product of the invention.

### Example 1

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**[0033]** 14.84 grams of cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were dissolved in 100 ml of water and the solution was kept under stirring. 100 ml of a solution of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) 15% w/w was prepared, placed in a burette and slowly added to the cobalt nitrate solution. The addition of carbonate was continued until the pH reached was 9. The solid was filtered off and washed with 250 ml of water at 15 °C. It was dried at 100 °C for 16 h and calcined at 400 °C for 2 h, to obtain a catalyst with the formula Co<sub>3</sub>O<sub>3.88</sub>K<sub>0.08</sub>.

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### Example 2

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**[0034]** When a sample of the material obtained according to example 1 was introduced into a tubular reactor and a gas stream of Ar with an N<sub>2</sub>O concentration of 1400 ppm, was fed at a ratio (Gas flow rate : catalyst volume) GHSV = 50,300 h<sup>-1</sup>, gradual heating of the gases inside the reactor resulted in a progressive decrease of the N<sub>2</sub>O concentration at the reactor outlet equivalent to N<sub>2</sub>O conversion values of 73 % at 260 °C, 95 % at 280 °C and 98 % at temperatures above 310 °C.

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**[0035]** When a sample of this material was introduced into a tubular reactor and a gas stream of Ar with an N<sub>2</sub>O concentration equal to 1400 ppm and O<sub>2</sub> = 3% v/v was fed at a ratio (total gas flow rate : catalyst volume) GHSV = 50,300 h<sup>-1</sup>, gradual heating of the gases inside the reactor resulted in a progressive decrease of the N<sub>2</sub>O concentration at the reactor outlet, equivalent to N<sub>2</sub>O conversion values of 17 % at 250 °C, 88 % at 300 °C and 96 % at temperatures above 350 °C.

**[0036]** When a sample of this material was introduced into a tubular reactor and a gas stream of Ar with an N<sub>2</sub>O

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concentration equal to 1400 ppm and  $[H_2O] = 0.5\%$  v/v was fed at a ratio (Total gas flow rate : catalyst volume) GHSV =  $50,300\text{ h}^{-1}$ , gradual heating of the gases inside the reactor resulted in a progressive decrease of the  $N_2O$  concentration at the reactor outlet, equivalent to  $N_2O$  conversion values of 25% at  $250^\circ\text{C}$ , 75% at  $280^\circ\text{C}$  and 98% at temperatures above  $340^\circ\text{C}$ .

5 [0037] When a sample of the material obtained according to example 1 was introduced into a tubular reactor and a gas stream of Ar with a concentration of  $N_2O$  equal to 1400 ppm,  $[O_2] = 3\%$  v/v and  $H_2O = 0.5\%$  v/v was fed at a ratio (Total gas flow : catalyst volume) GHSV =  $50,300\text{ h}^{-1}$ , gradual heating of the gases inside the reactor resulted in a progressive decrease of the  $N_2O$  concentration at the reactor outlet, equivalent to  $N_2O$  conversion values of 17 % at  $260^\circ\text{C}$ , 42 % at  $275^\circ\text{C}$ , 73 % at  $290^\circ\text{C}$ , 94% at  $315^\circ\text{C}$  and 97 % at temperatures above  $350^\circ\text{C}$ .

10 [0038] When a sample of the material obtained according to example 1 was introduced into a tubular reactor and a stream of Ar gas was fed, with a concentration of  $N_2O$  equal to 1400 ppm,  $[O_2] = 3\%$  v/v and  $H_2O = 0.5\%$  v/v, at a ratio (Total gas flow : catalyst volume) GHSV =  $50,300\text{ h}^{-1}$ , keeping the reaction temperature equal to  $360^\circ\text{C}$ , an initial  $N_2O$  conversion of 93% was obtained, experiencing a slight increase in conversion to 96% over 65 hours in reaction.

### 15 Example 3

[0039] 14.84 grams of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were dissolved in 100 ml of water and the solution was kept under stirring. 100 ml of a solution of caesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) at 30% w/w was prepared. This solution was poured into a burette. The carbonate solution was slowly added and maintained until the pH reached was 9. The total volume of carbonate added was 57.5 ml. The solid was filtered off and washed with 220 ml of water at  $15^\circ\text{C}$ . It was dried at  $100^\circ\text{C}$  for 16 h and calcined at  $400^\circ\text{C}$  for 2 h to obtain a material with the formula  $\text{Co}_3\text{O}_{3.88}\text{Cs}_{0.15}$ .

### Example 4

25 [0040] When a sample of the material obtained according to example 3 was introduced into a tubular reactor and a gas stream of Ar with a concentration of  $N_2O$  equivalent to 1400 ppm,  $[O_2] = 3\%$  v/v and  $H_2O = 0.5\%$  v/v was fed at a ratio (Total gas flow : catalyst volume) GHSV =  $50,300\text{ h}^{-1}$ , gradual heating of the gases inside the reactor resulted in a progressive decrease of the  $N_2O$  concentration at the reactor outlet equivalent to  $N_2O$  conversion values of 50 % at  $280^\circ\text{C}$ , 80 % at  $300^\circ\text{C}$ , 93 % at  $320^\circ\text{C}$  and 97 % at temperatures above  $340^\circ\text{C}$ .

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### Example 5

[0041] 59.36 grams of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were dissolved in 400 ml of water and the solution was kept under stirring. 400 ml of a solution of caesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) at 30% w/w was prepared. This solution was poured into a burette. The carbonate solution was slowly added and maintained until the pH reached was 9. The total volume of carbonate added was 207 ml. The solid was filtered off and washed with 1160 ml of water at  $15^\circ\text{C}$ . It was dried at  $100^\circ\text{C}$  for 16 h and calcined at  $400^\circ\text{C}$  for 2 h to obtain a material with the formula  $\text{Co}_3\text{O}_{3.88}\text{Cs}_{0.06}$ .

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### Example 6

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[0042] When a sample of the material obtained according to example 5 was introduced into a tubular reactor and a gas stream of Ar with a concentration of  $N_2O$  equivalent to 1400 ppm,  $[O_2] = 3\%$  v/v and  $H_2O = 0.5\%$  v/v was fed at a ratio (Total gas flow : catalyst volume) GHSV =  $24,000\text{ h}^{-1}$ , gradual heating of the gases inside the reactor resulted in a progressive decrease of the  $N_2O$  concentration at the reactor outlet equivalent to  $N_2O$  conversion values of 47 % at  $250^\circ\text{C}$ , 88 % at  $280^\circ\text{C}$ , 95 % at  $300^\circ\text{C}$  and 99 % at temperatures above  $320^\circ\text{C}$ .

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### Example 7

[0043] 14.84 grams of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were dissolved in 100 ml of water and the solution was kept under stirring. 100 ml of a solution of potassium carbonate ( $\text{K}_2\text{CO}_3$ ) at 15 % w/w was prepared, placed in a burette and the potassium carbonate solution was slowly added to the cobalt nitrate solution and the addition of carbonate was continued until the pH reached was 9. The total volume of carbonate added was 54 ml. The solid was filtered off and washed with 400 ml of water at  $15^\circ\text{C}$ . It was dried at  $100^\circ\text{C}$  for 16 h and calcined at  $400^\circ\text{C}$  for 2 h, obtaining a K-free material with the formula  $\text{Co}_3\text{O}_4$ .

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### Example 8

[0044] When a sample of the material obtained according to example 7 was introduced into a tubular reactor and an

Ar gas stream with an N<sub>2</sub>O concentration equivalent to 1400 ppm was fed at a ratio (Gas flow rate : catalyst volume) GHSV = 50,300 h<sup>-1</sup>, gradual heating of the gases inside the reactor resulted in a progressive decrease of the N<sub>2</sub>O concentration at the reactor outlet, equivalent to N<sub>2</sub>O conversion values of 9 % at 280 °C, 20 % at 320 °C, 34 % at 360 °C and 44 % at 380 °C. A decrease in N<sub>2</sub>O conversion due to the absence of the alkaline element was observed throughout the range of temperature tested.

### Example 9

**[0045]** X-ray diffractograms (XRD) of the materials described in examples 1 and 3 show that these materials have a cubic structure close to that of the Co<sub>3</sub>O<sub>4</sub> spinel described in example 7 (JCPDS 00-042-1467) (Figure 1). The average crystallite size was calculated according to the Scherrer equation respectively obtaining values around 18 nm and 10 nm.

**[0046]** Scanning Electron Microscopy micrographs of these materials (Figure 2) showed an average primary particle size between 10 and 20 nm for example 1 and 8-15 nm for example 3.

**[0047]** These microphotographs show the general surface appearance of the materials, formed by agglomerates of primary particles with sizes similar to those obtained for crystallite sizes by XRD, and with pores whose diameter falls within the range of mesoporous materials (2-50 nm), as determined by N<sub>2</sub> adsorption-desorption isotherms (Figure 3).

### Example 10

**[0048]** The samples of the materials described in examples 1 and 7 were analysed by X-ray photoelectron spectroscopy (XPS) showing a shift of the Co 2p level in the sample Co<sub>3</sub>O<sub>3.88</sub>K<sub>0.08</sub> (example 1) towards lower binding energies with respect to the sample without K (example 7) which is explained by the increase in the proportion of Co(II) (CoO) species that are stabilised by the electron donation effect promoted by the presence of K<sup>+</sup> ions (figure 4).

**[0049]** According to these results, the material obtained following the procedure described in the invention is clearly different, as regards its redox properties, with respect to those previously described.

### Example 11

**[0050]** Programmed temperature reduction experiments were performed on the materials described in examples 1 and 3, detecting a shift of the first reduction peak towards lower temperatures (246 and 262 °C respectively for Co<sub>3</sub>O<sub>3.88</sub>K<sub>0.08</sub> and Co<sub>3</sub>O<sub>3.88</sub>Cs<sub>0.15</sub>) compared to those reported in the state of the art for conventional spinel (Figure 5). From these results, the Co<sup>2+</sup>/Co<sup>3+</sup> ratio was calculated, obtaining a value higher than the stoichiometric value (0.7 versus 0.5). This increase in the ratio of Co(II) with respect to Co(III) in the spinel lattice leads to the appearance of a certain proportion of oxygen vacancies, which give the surface of the material special properties for adsorbing and activating the N<sub>2</sub>O molecule. This changes the stoichiometry of the spinel, making it oxygen deficient.

**[0051]** According to these results, the material obtained following the procedure described in the invention is clearly different, as regards its redox properties, with respect to those previously described.

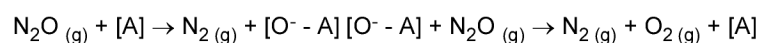
### Example 12

**[0052]** O<sub>2</sub> temperature-programmed desorption (O<sub>2</sub>-TPD) experiments were performed with the materials described in examples 1, 3 and 7. In the materials whose washing was controlled (examples 1 and 3), the peak relative to surface oxygen (P<sub>O<sub>2</sub>-I</sub>) appeared at temperatures around 100 °C (figure 6), compared to 190 °C for the material without K (example 7).

**[0053]** Furthermore, the peak relative to the lattice oxygen (P<sub>O<sub>2</sub>-II</sub>) shifted to lower temperatures (180 - 350 °C) whereas in the K-free spinel this peak appeared from 300 °C onwards.

**[0054]** Based on these results, it can be concluded that the materials covered by this patent are clearly different in terms of their O<sub>2</sub> adsorption/desorption capacity.

**[0055]** The most accepted mechanism for the N<sub>2</sub>O decomposition reaction is through adsorption of N<sub>2</sub>O on an active centre [A], releasing N<sub>2</sub> and leaving an O atom adsorbed on that centre. A second N<sub>2</sub>O molecule is adsorbed on this centre, giving rise to another N<sub>2</sub> molecule. The two adsorbed O atoms must recombine to form molecular O<sub>2</sub>, this being the limiting stage of the reaction:



**[0056]** The O<sub>2</sub> DTP results obtained show that the samples described in examples 1 and 3 have the ability to perform the O<sub>2</sub> desorption processes from the lattice oxygen (P<sub>O<sub>2</sub>-II</sub>) at a temperature (200 - 300°C) significantly lower than that required by the sample with conventional spinel structure (> 300°C). This can be considered to be related to the lowering

of the temperature required by these new catalysts to carry out the N<sub>2</sub>O decomposition process under the indicated conditions.

### Example 13

**[0057]** A comparison is made of the data obtained from the catalyst obtained according to example 1 of the present invention against the data described in the prior art documents, "D1" [Li Xue, Changbin Zhang, Hong He, Yasutake Teraoka, Applied Catalysis B: Environmental, Volume 75, Issues 3-4, 2007, Pages 167-174, figure 8], where, for instance, at 350 °C, it is possible to observe that the conversion obtained with this catalyst, under conditions of humidity and the presence of O<sub>2</sub>, is close to 77%, compared to the 96% conversion obtained with the Co<sub>3</sub>O<sub>3.88</sub>K<sub>0.08</sub> material. To compare these results, the data have been analysed as a function of the space velocity (GHSV) at which the different experiments have been carried out. Figure 7 shows the results of N<sub>2</sub>O conversion under conditions of humidity and in the presence of O<sub>2</sub> for the mentioned catalysts as a function of space time or contact time, i.e. considering the volume of the catalyst and the flow rate used in each experiment ( $T = V_{\text{cat}}/F = 1/\text{GHSV}$ ). This comparison highlights the great improvement in the catalytic activity of this material compared to the state of the art since a shorter contact time (lower volume of catalyst) is needed to achieve similar or higher conversions.

**[0058]** The following table shows the values of the reaction constant at 350°C, K<sub>350°C</sub>, calculated considering that the reaction runs according to a first-order kinetics, which would be the best quantitative expression of the catalytic activity.

Table 1. Values of the reaction constant of the catalysts.

Catalyst	1st order eq.
	K <sub>350°C</sub> (s <sup>-1</sup> )
Co <sub>3</sub> O <sub>3.88</sub> K <sub>0.08</sub>	45.0
Cat Co <sub>3</sub> O <sub>4</sub> (D1)	2.9

**[0059]** According to these data, the increase in reaction rate produced by the catalysts covered by the patent is more than an order of magnitude greater than the best described in the article mentioned in this example.

**[0060]** On the other hand, the catalyst described in this article, D1, as Co<sub>3</sub>O<sub>4</sub>, showed a binding energy of the Co 2p 3/2 component of 780.1 eV similar to the K-free spinel described in example 7 (Figure 3), and the desorption of the lattice oxygen obtained by O<sub>2</sub> DTP takes place, as with the K-free spinel described in example 7, at 300°C and above (Figure 5).

### Example 14

**[0061]** The material obtained according to example 1 and according to example 3 of the present invention and the data shown in the prior art document, "D2" [Pawet Stelmachowski, Gabriela Maniak, Andrzej Kotarba, Zbigniew Sojka, Catalysis Communications, Volume 10, Issue 7, 2009, Pages 1062-1065, Figure 7] are compared. It can be seen from Figure 7 of "D2" that under humid conditions (option b) the Cs-doped catalyst achieves a conversion value close to 90 % at 350 °C. The K-doped catalyst is significantly less active, since at this temperature the estimated conversion in this curve is close to 50%, while the conversion of the materials in examples 1 and 5 is respectively 96 and 98%, using a much smaller volume of catalyst (shorter contact time).

**[0062]** Furthermore, the following table shows the values of the reaction constant at 350 °C, K<sub>350°C</sub>, calculated considering that the reaction runs according to a first-order kinetics, which would be the best quantitative expression of the catalytic activity.

Table 2. Values of the reaction constant of the catalysts.

Catalyst	1st order eq.
	K <sub>350°C</sub> (s <sup>-1</sup> )
Co <sub>3</sub> O <sub>3.88</sub> K <sub>0.08</sub>	45.0
Co <sub>3</sub> O <sub>3.88</sub> Cs <sub>0.15</sub>	49.0
Cat Cs (D2)	4.3

**[0063]** According to these data, the increase in reaction rate produced by the materials covered by the patent is more

than an order of magnitude greater than the best described in the article mentioned in this example.

## Claims

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1. A material **characterised in that** it has a non-stoichiometric spinel-type crystal structure with the general formula  $\text{Co}_3\text{O}_{4-x/2}\text{A}_y$ , wherein:

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x has a value between 0.02 and 0.3

A is an alkali element, and

y has a value of between 0.06 and 0.18

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with an A/Co ratio between 0.02 and 0.10; a  $\text{Co}^{2+}/\text{Co}^{3+}$  ratio between 0.55 and 0.80; and a primary particle size equivalent to the crystallite size between 5 and 30 nm.

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2. The material according to claim 1, wherein the material has a specific surface area BET of between 40  $\text{m}^2/\text{g}$  and 80  $\text{m}^2/\text{g}$ .

3. The material according to any one of claims 1 or 2, wherein the material has a pore volume of between 0.2  $\text{cm}^3/\text{g}$  and 0.4  $\text{cm}^3/\text{g}$ .

4. The material according to any one of claims 1 to 3, wherein the material is mesoporous.

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5. The material according to any one of claims 1 to 4, wherein the alkali element A is K, x is 0.182, and y is 0.09.

6. The material according to any one of claims 1 to 4, wherein the alkali element A is Cs, x is 0.235, and y is 0.15.

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7. A process for obtaining the material according to claims 1 to 6, **characterised in that** it comprises the following steps:

a) dissolving a cobalt salt in water;

b) dissolving an alkali metal salt or hydroxide in water;

c) slowly adding the solution obtained in step (b) to the solution prepared in step (a) until a pH of between 8 and 11 is reached;

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d) filtering the solid obtained in step (c) and washing it with 5 ml to 75 ml of water for each gram of cobalt salt added in step (a);

e) drying the solid obtained in step (d) at a temperature between 50 °C and 200 °C for a time between 12 h and 20 h; and

f) calcining the solid obtained in step (e) at a temperature between 200 °C and 700 °C in an air atmosphere for at least 30 min.

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8. The process according to claim 7, wherein the cobalt salt in step (a) is selected from cobalt nitrate hexahydrate, cobalt sulphate, cobalt chloride and cobalt acetate.

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9. The process according to any one of claims 7 or 8, wherein the alkali metal salt or hydroxide in step (b) is selected from alkali metal carbonate, alkali metal nitrate, alkali metal hydroxide and alkali metal acetate.

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10. The process according to claim 9, wherein if the cobalt salt is cobalt nitrate hexahydrate and the alkali metal salt is alkali metal carbonate, the washing of step (d) is with an amount of water between 16 ml/g and 21 ml/g of cobalt nitrate hexahydrate.

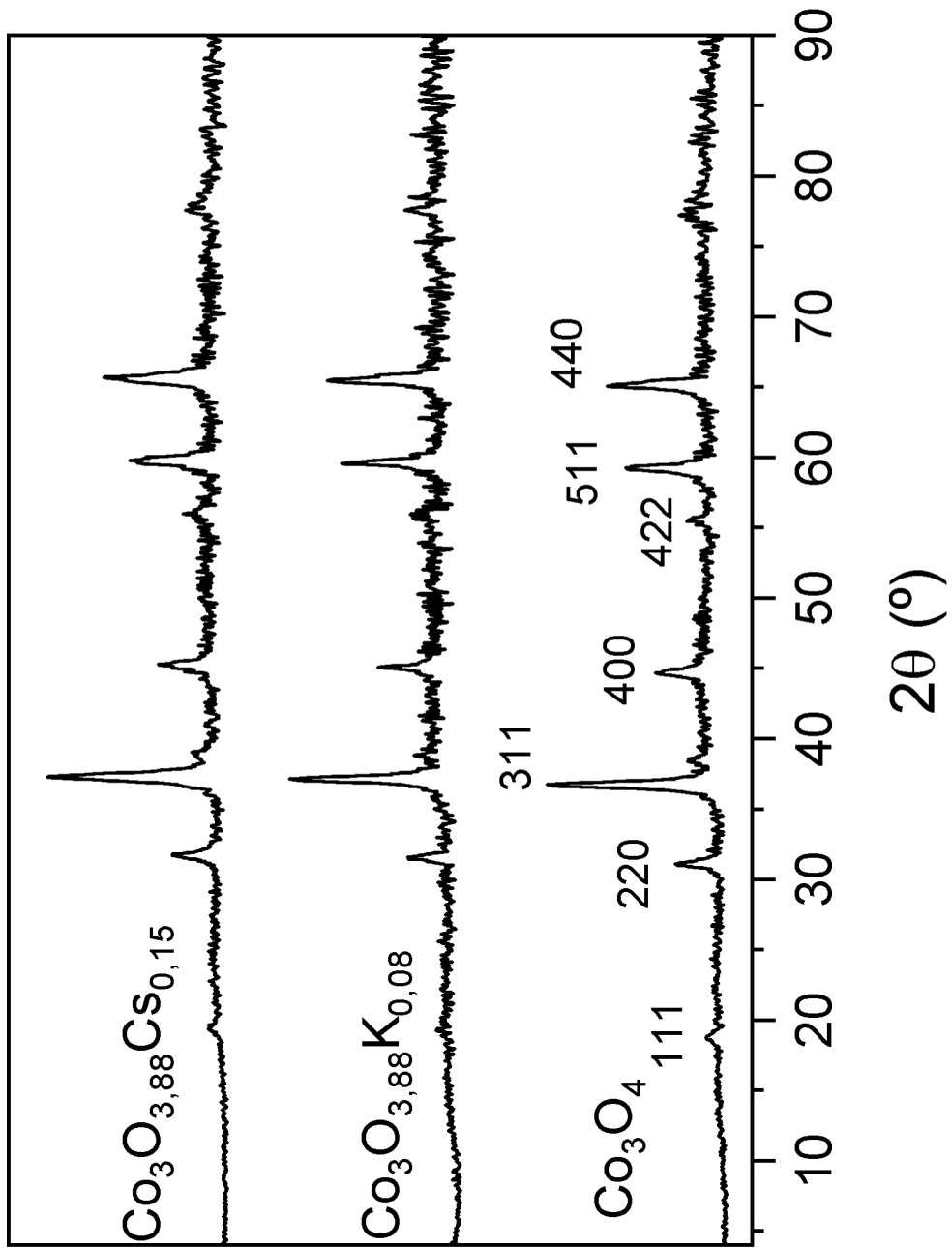
11. Use of the material according to any one of claims 1 to 6 as a catalyst.

12. Use of the material according to claim 11 as a catalyst in the oxidation/decomposition of gases.

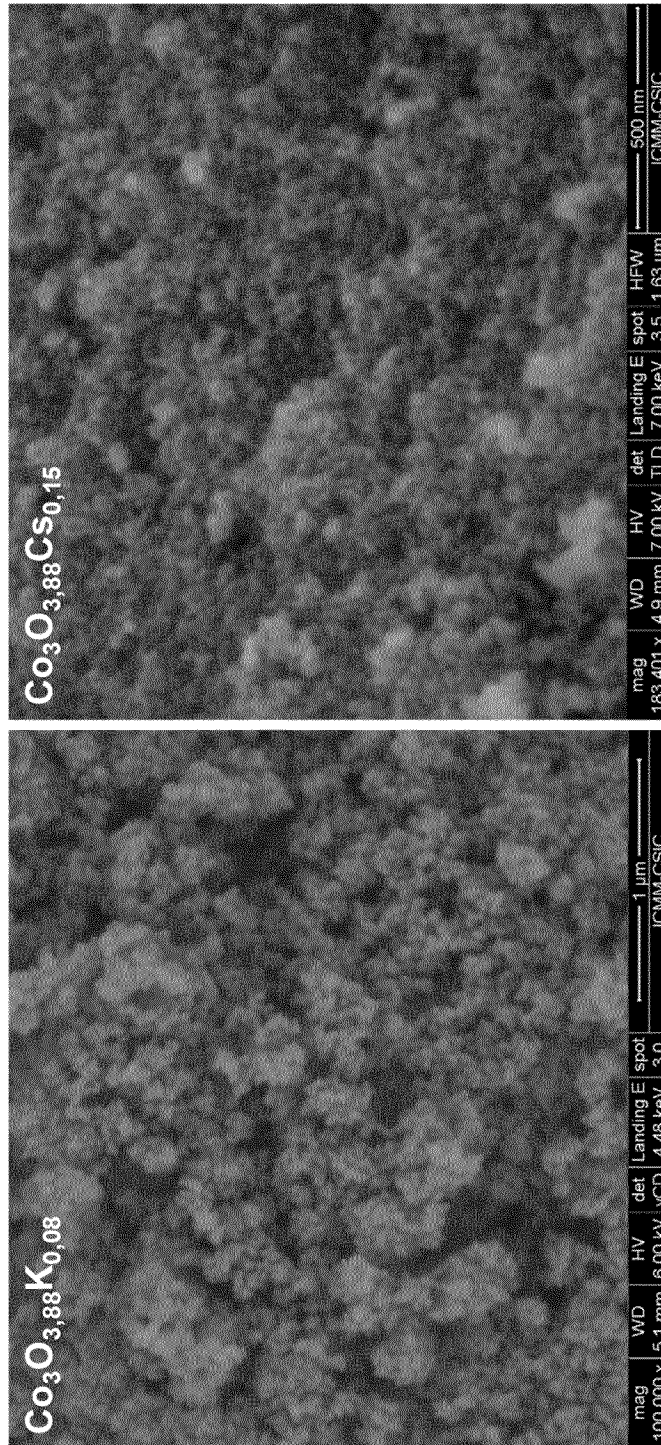
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13. Use of the material according to claim 11 as a catalyst for the decomposition of  $\text{N}_2\text{O}$ .

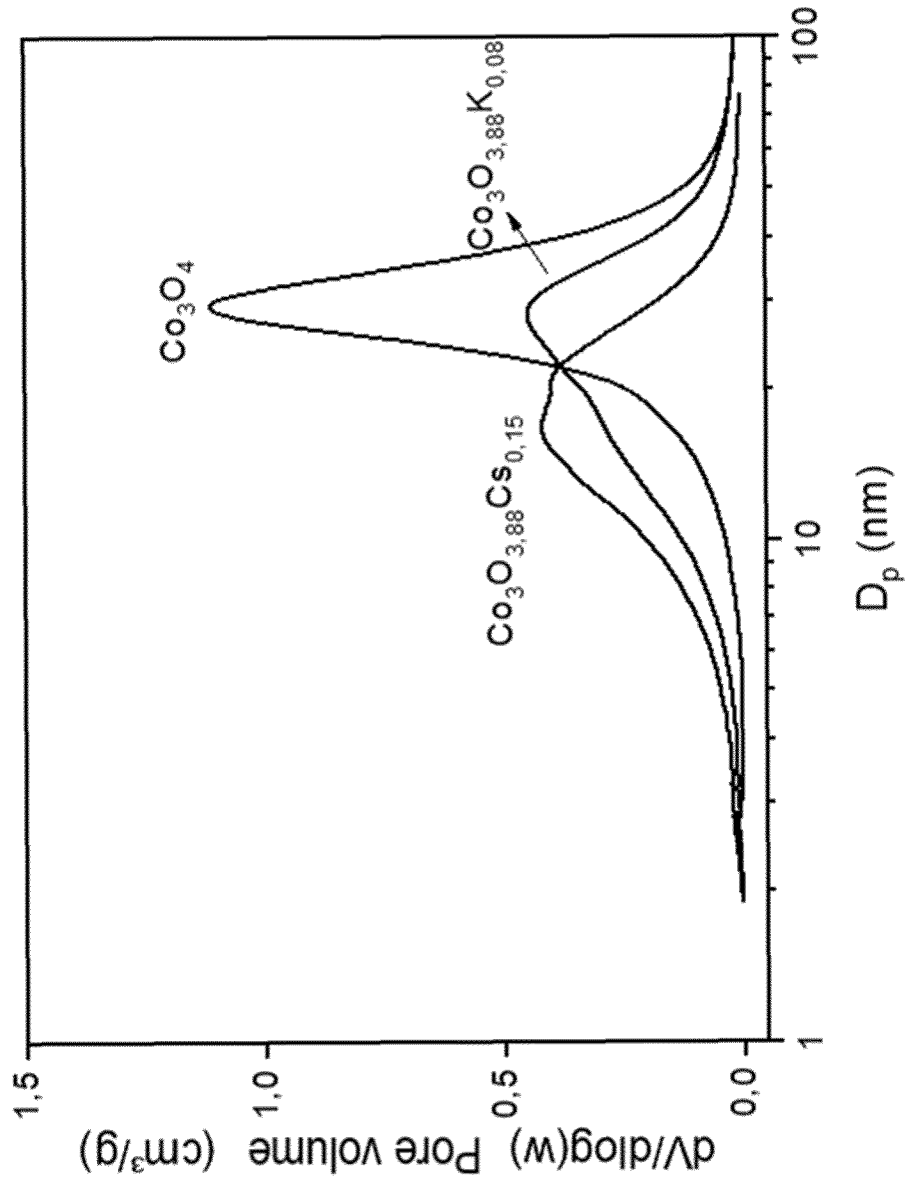




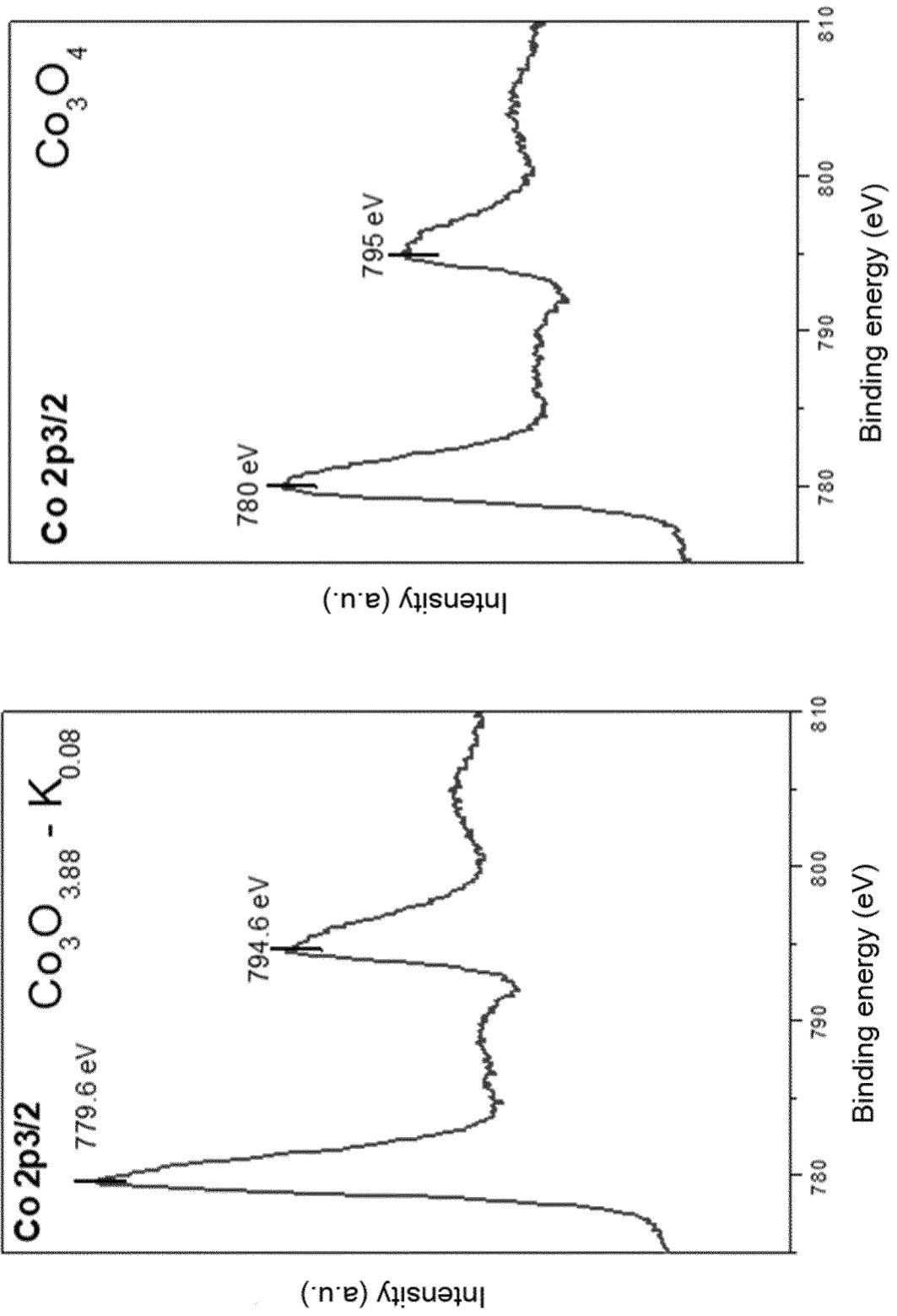
**Fig. 1**



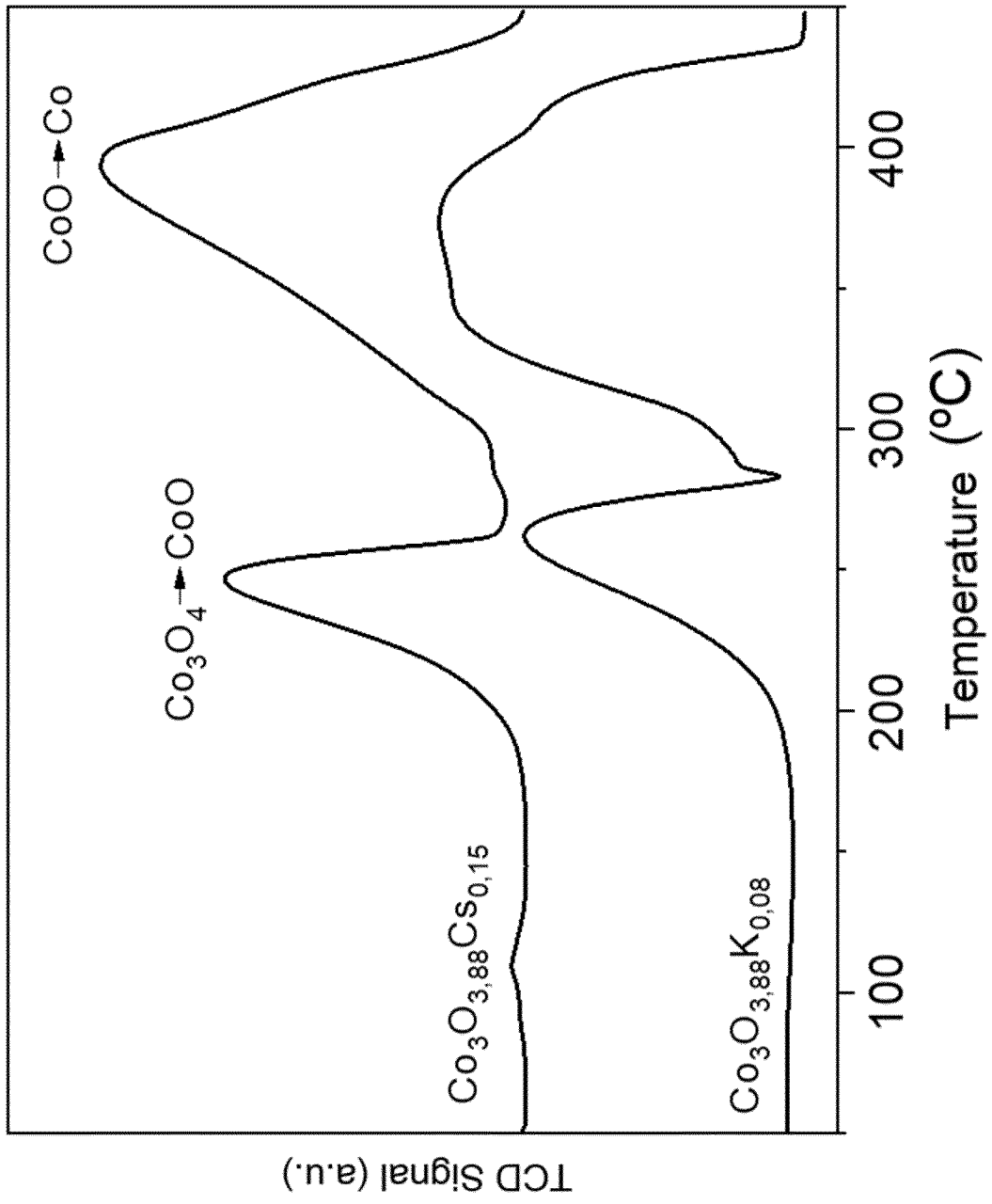
**Fig. 2**

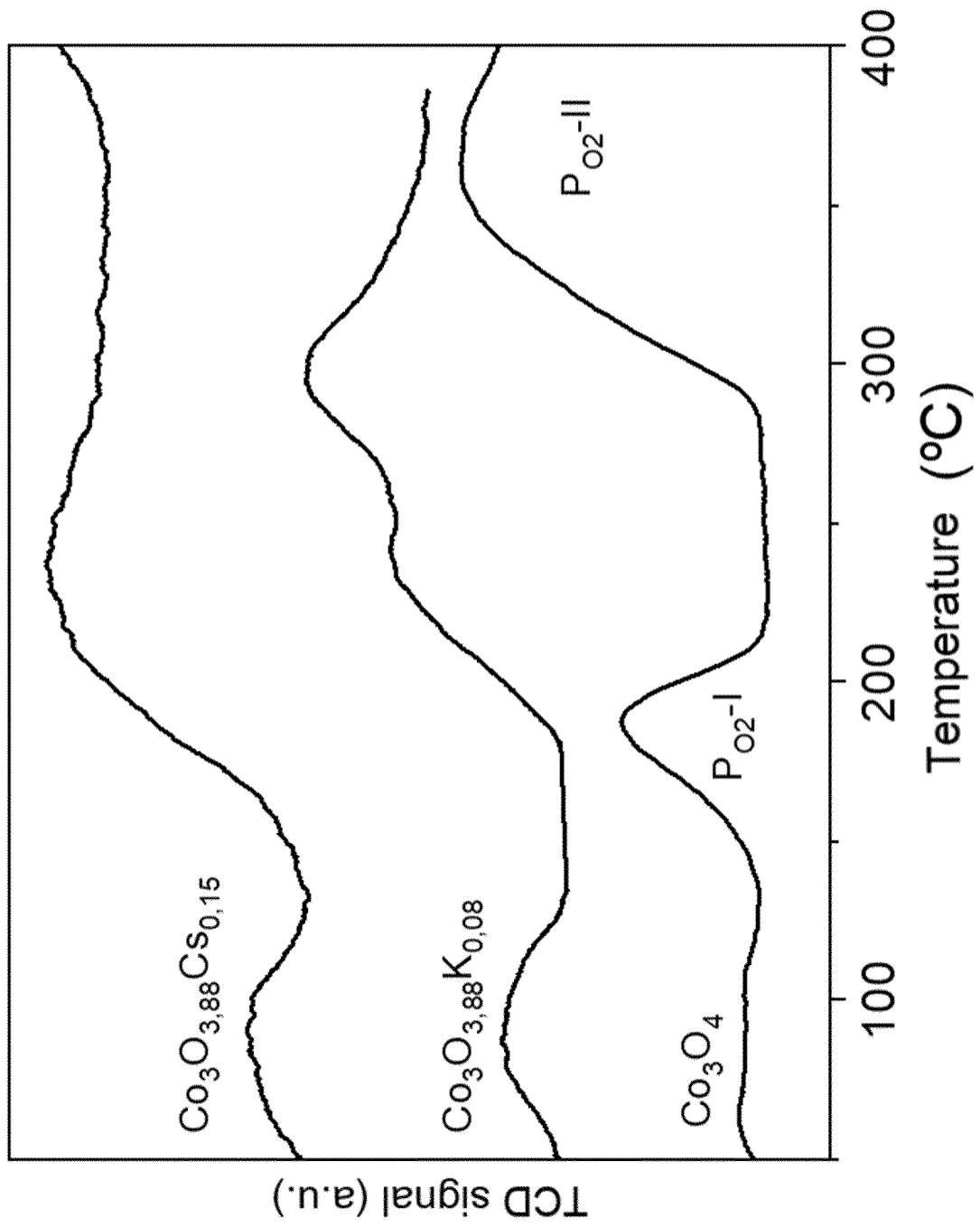


**Fig. 3**



**Fig. 4**

**Fig. 5**

**Fig. 6**

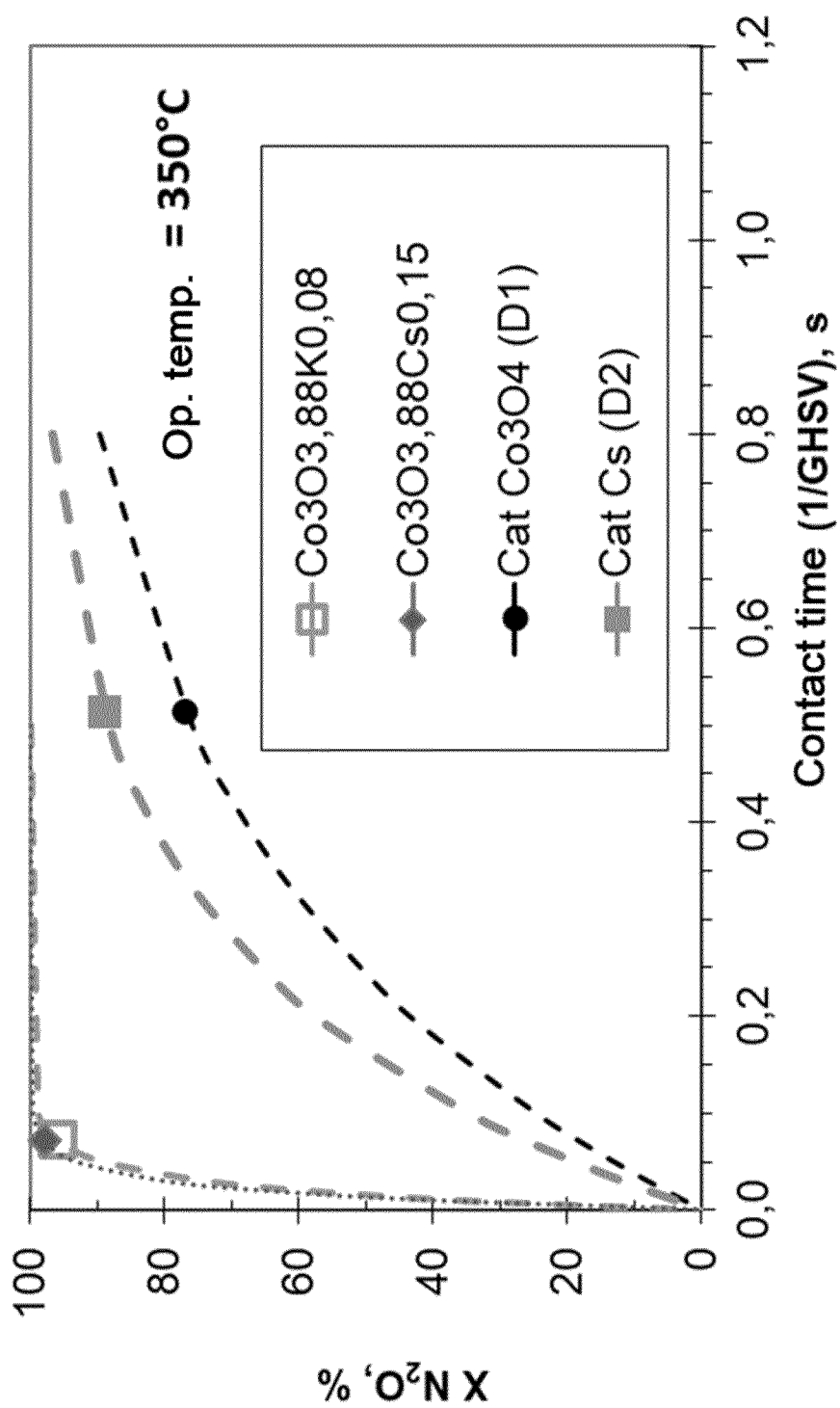


Fig. 7

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2021/070138

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## A. CLASSIFICATION OF SUBJECT MATTER

**B01J23/78** (2006.01)**B01J23/75** (2006.01)

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

## B. FIELDS SEARCHED

10

Minimum documentation searched (classification system followed by classification symbols)

B01J

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

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

INVENES, EPODOC, WPI, TXPUS, TXPWO, TXPCN, TXPSPJ, TXPSPK, NPL, COMPENDEX, INSPEC, GOOGLE, GOOGLE PATENT, GOOGLE SCHOLAR.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WÓJCIK, SYLWIA, et al. Bulk, surface and interface promotion of Co <sub>3</sub> O <sub>4</sub> for the low-temperature N <sub>2</sub> O decomposition catalysis. Catalysts, 30/12/2019, Vol. 10, N° 41, pages 1-15 2.2.2 Surface promotion, 4.1. Co3O4-Based Promoted Catalysts.	1-13
A	JP 2007054714 A (UNIV KYOTO ET AL.) 08/03/2007, paragraphs [0007-0010], [0019], [0022-0031], Examples 3, 4, 11, 17.	1-13
A	JP 2012050969 A (NIPPON CATALYTIC CHEM IND) 15/03/2012, paragraphs [0008-0019], [0025-0028], Example 1.	1-13

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 Further documents are listed in the continuation of Box C. See patent family annex.

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\* Special categories of cited documents:

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"E" earlier document but published on or after the international filing date

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"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

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Date of the actual completion of the international search

17/06/2021

Date of mailing of the international search report

(18/06/2021)

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2021/070138

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C (continuation).		DOCUMENTS CONSIDERED TO BE RELEVANT
Category *	Citation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
10 A	ASANO et al. Potassium-doped Co <sub>3</sub> O <sub>4</sub> catalyst for direct decomposition of N <sub>2</sub> O. Applied Catalysis B: Environmental, 21/12/2007, Vol. 78, N° 3-4, pages 242 - 249, <DOI: 10.1016/j.apcatb.2007.09.016>. 2.1 Preparation of Co <sub>3</sub> O <sub>4</sub> catalyst.	1-13
15 A	STELMACHOWSKI P et al. Strong electronic promotion of Co <sub>3</sub> O <sub>4</sub> towards N <sub>2</sub> O decomposition by Surface alkali dopants. Catalysis Communications, 10/03/2009, Vol. 10, N° 7, pages 1062 - 1065, <DOI:10.1016/j.catcom.2008.12.057>. 2. Experimental, 3. Results and discussion.	1-13
20 A	PASHA N et al. Studies on cesium doped cobalt oxide catalysts for direct N <sub>2</sub> O decomposition in the presence of oxygen and steam. Catalysis Communications, 15/11/2008, Vol. 10, N° 2, pages 132 - 136, <DOI: 10.1016/j.catcom.2008.06.006>. 2. Experimental, 3. Results and discussion.	1-13
25 A	ZASADA F et al. Potassium promotion of cobalt spinel catalyst for N <sub>2</sub> O decomposition-accounted by work function measurements and DFT modelling. Catalysis Letters January, 31/12/2008, Vol. 127, N° 1-2, pages 126 - 131, <DOI: 10.1007/s10562-008-9655-6>. 2. Experimental.	1-13
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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/ES2021/070138

Information on patent family members

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Patent document cited in the search report	Publication date	Patent family member(s)	Publication date
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----- JP2012050969 A	----- 15.03.2012	----- JP5483723B B2	----- 07.05.2014

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## REFERENCES CITED IN THE DESCRIPTION

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