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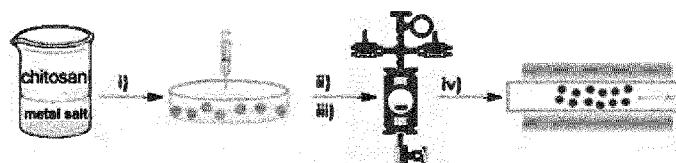
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(54) Title: PREPARATION METHOD FOR PREPARING A CATALYST BASED ON IRON NANOPARTICLES, COBALT NANOPARTICLES OR ALLOYS THEREOF, THE CATALYST THUS PREPARED AND USE OF THE CATALYST FOR THE SELECTIVE HYDROGENATION OF CARBON DIOXIDE TO ISOBUTANE

FIG. 1



(57) Abstract: The present invention describes a preparation method for preparing a catalyst made up of a Fe and Co metal alloy in several ratios in the form of nanoparticles embedded in a graphitic carbon matrix. Another object of the invention is also the prepared catalyst which in a surprising manner selectively catalyses the hydrogenation of carbon dioxide into isobutane.



PREPARATION METHOD FOR PREPARING A CATALYST BASED ON IRON NANOPARTICLES, COBALT NANOPARTICLES OR ALLOYS THEREOF, THE CATALYST THUS PREPARED AND USE OF THE CATALYST FOR THE SELECTIVE HYDROGENATION OF CARBON DIOXIDE TO ISOBUTANE

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DESCRIPTION

The present invention describes a preparation method for preparing a catalyst made up of an Fe and Co metal alloy in several ratios in the form of nanoparticles embedded in a carbon matrix. Another object of the invention is also the prepared catalyst which in a surprising manner selectively catalyses the hydrogenation of carbon dioxide into isobutane.

BACKGROUND OF THE INVENTION

15 Stemming from international agreements to reduce greenhouse effect gas emissions, and more specifically to reduce atmospheric carbon dioxide (CO₂) emissions, there is an interest in converting this gas into products that can serve as fuels or compounds for the chemical industry.

20 Given that CO₂ is one of the most thermodynamically stable molecules, most reactions that can be considered for converting CO₂ are thermodynamically unfavourable, therefore giving rise to products with low or very low yields.

An exception to this general rule is the reaction of CO₂ with hydrogen, which can be thermodynamically favourable depending on the formed product or products. Among possible hydrogenation reactions, one of the most common ones is CO₂ methanation (equation 1) also known as the Sabatier reaction, named after the French scientist who studied it. Other hydrogenation reactions which are also thermodynamically favourable give rise to other products, particularly saturated and unsaturated hydrocarbons and alcohols. The hydrogen necessary for these reactions may come from water by electrolysis, thermolysis, biomass or from any other origin, being of particular importance in this case those forms of preparing hydrogen that do not generate CO₂ emissions and use renewable energies, particularly electricity of a wind origin, photovoltaic origin, hydraulic origin or other renewable sources.



Although hydrogenation reactions of CO₂ are thermodynamically spontaneous,
5 and since they are exothermal equilibriums are more favourable at low
temperatures, the speeds of all these hydrogenation reactions of CO₂ are very
low in the range of temperatures between 300 and 600 °C. These low reaction
speeds are due to the high activation energies needed to promote the reactivity
of molecules with bonds as strong as CO₂ and H₂. Catalysts which accelerate the
10 reaction and direct the selectivity of the process towards certain products are
therefore required.

Among catalysts for carrying out CO₂ methanation, one of the most common is
formed by nickel nanoparticles supported in alumina or silica-alumina. Other
15 catalysts that have been studied are similar to those used in the Fischer-Tropsch
reaction of synthesis gas, which are formed on the basis of iron or cobalt or even
alloys of both. Tavasoli, A. et al. *Fischer_Tropsch synthesis on mono- and
bimetallic Co and Fe catalysts supported on carbon nanotube*; Fuel Processing
Technology Vol. 90, Issue 12, (2009), 1486-1494 refers to mono- and bimetallic
20 cobalt and iron catalysts supported on carbon nanotubes. Said catalysts are
obtained by a method of incipient wetness impregnation from cobalt and iron
nitrates.

The document of Gual, A. et al. *Colloidal Ru, Co and Fe-nanoparticles. Synthesis
25 and application of nanocatalysts in the Fischer-Tropsch process*; Catalysis Today
Vol. 183, Issue 1, (2012), 154-171 discloses the synthesis of cobalt and iron
nanoparticles with sizes comprised between 5.5 and 6.3 nm and stabilised with
cellulose for use as catalysts in the hydrogenation of carbon monoxide.

30 These iron catalysts give rise to hydrocarbon mixtures, typically between C1 to
C4, methane being the most abundant component and the percentage of product
dropping abruptly with the number of carbon atoms. In the case of cobalt, the
product formed with high selectivity is, again, methane. In the case of both iron
and cobalt, the nanoparticles of these metals have been supported on metallic
35 oxides such as the alumina, which may or may not contain a promoter the

function of which is to increase the selectivity of the product mixture. Among the most used promoters are potassium and manganese. Iron and cobalt alloys can likewise promote the hydrogenation reaction, C1-C4 product mixtures being formed.

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Among the examples described in the literature, T. Yisheng et al. *Syntheses of Isobutane and Branched Higher Hydrocarbons from Carbon Dioxide and Hydrogen over Composite Catalysts* Ind. Eng. Chem. Res. (1999), 38, 3225-3229 describe that iron nanoparticles in acidic Y zeolite may selectively give rise to isobutane formation. However, this selective catalyst undergoes rapid deactivation due to the deposition of coke on its surface and does not possess any practical usefulness.

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DESCRIPTION OF THE INVENTION

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In a first aspect, the object of the present invention is a preparation method for preparing a catalyst based on iron nanoparticles, cobalt nanoparticles or alloys thereof embedded in a graphitic carbon matrix, characterised in that it comprises the following steps:

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a. forming a hydrogel by adding an aqueous solution of a natural biopolymer to a solution containing at least an Fe salt, a Co salt or mixtures of Fe and Co salts in a range of Fe/Co atomic ratios comprised between 0.1 and 1,

25

b. converting the hydrogel obtained in the preceding step into an alcogel by the gradual replacement of water with an alcohol which is selected from ethanol, methanol or propanol by suspending the hydrogel in a successive series of ethanol-water mixtures at ratios comprised between 10:90 and 100:0,

30

c. drying the alcogel resulting from the preceding step to obtain a dry aerogel mass by using supercritical CO₂,

d. pyrolysing the dry aerogel in the absence of oxygen in a range of temperatures between 800 and 1200 °C,

e. transforming the residues from pyrolysis into a material where the particle size of metallic oxide is comprised between 0.5 nm and 100 nm, preferably of between 2 nm and 20 nm.

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The term "hydrogel" in the present invention refers to the wet biopolymer precipitate containing the iron and cobalt species.

- 5 The term "alcogel" in the present invention refers to the dehydrated gel containing an alcohol.

The term "aerogel" in the present invention refers to the alcogel dried by supercritical CO₂.

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In a preferred embodiment of the method of the invention:

- the biopolymer is a natural polysaccharide which is selected from chitosan, alginic acid, alkaline and alkaline earth metal alginate, carrageenan and mixtures at any ratio of any combination thereof;
- 15
- the ratio between the natural biopolymer and the Fe salt, Co salt or mixture of Fe and Co salts is comprised between 100 and 100,000;
 - the Fe or Co salt is selected from Fe or Co acetate, nitrate, chloride or salt complexes with ammonia.
- 20 As for the pyrolysis conditions in the absence of oxygen, this can be performed:
- under vacuum conditions at a pressure of less than 10⁻³ mmHg
 - in the presence of a flow of an inert gas which is selected from N₂, Ar, He or mixtures thereof.
- 25 Pyrolysis is programmed at an initial speed of 1 °C/min until reaching 200 °C, which is maintained for 2 h and subsequently raised to 900 °C which is maintained for 2 h, followed by cooling with the absence of oxygen being maintained.
- 30 The transformation of the residue from pyrolysis is carried out by means of a method which is selected from grinding, treatment with ultrasounds or mechanical agitation so as to be dispersed in a liquid medium which is subsequently eliminated by evaporation.
- 35 In a second aspect, the object of present invention is a catalyst prepared by

means of a method as has been described, characterised in that:

- the residual oxygen content is less than 20 %,
- the Fe and Co content is comprised between 0.05 % and 20 % by weight,
- 5 - it is in the form of metallic oxide nanoparticles having sizes comprised between 0.5 nm and 100 nm, preferably between 2 nm and 20 nm, embedded in a graphitic carbon matrix.

10 In particular embodiments, the carbon matrix of the catalyst contains a percentage of N equal to or less than 7 % when the biopolymer is chitosan and contains a percentage of S less than 10 % when the biopolymer is carrageenan.

15 In a third aspect, the object of the present invention is the use of a catalyst as described for the selective hydrogenation of carbon dioxide to isobutane. The preferred conditions for carrying this out are:

- the temperature comprised between 350 °C and 600 °C,
- the molar ratio between CO₂ and H₂ comprised between 1/2 and 1/7,
- pressure comprised between 100 and 2000 KPa.

20 **DETAILED DESCRIPTION OF THE INVENTION**

The present invention describes catalysts based on Fe and Co alloy nanoparticles supported on a carbon matrix which, under certain favourable reaction conditions, is capable of promoting the selective hydrogenation of CO₂ to isobutane. The selectivity and stability of these catalysts is unexpected taking into account the state of the art described above, where methane is the main product and hydrocarbon mixtures are always described.

30 The invention includes the manner of preparing these catalytic materials to achieve the activity that will be described and is summarised in diagram 1 of Figure 1.

35 These catalysts are prepared from aqueous solutions of 50 ml of iron(II) and Co(II) salts at a concentration between 0 and 1 g of Fe×L⁻¹ and between 0 and 1 g of Co×L⁻¹, respectively. Suitable of Fe and Co precursors in these

formulations are the respective acetates, chlorides and nitrates, but the present invention is not limited to these salts. In these cases, pH values must be adjusted to acidic values less than 5.

- 5 It is also possible to use either neutral or charged complexes of these transition metal cations as precursors, with the corresponding compensation anions being present in this second case. It is thus possible to use as precursors of these catalysts iron and cobalt salt complexes with ammonia in the form of tetraamino iron(II) chloride and tetraamino cobalt(II) chloride, among other possible
10 precursors. In these cases, the pH value of the solution must be compatible with the metallic species according to the state of the art.

The atomic ratio between Fe and Co varies in the solution in a preferred range of Fe/Co between 0.1 and 1.

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- A weight of a natural biopolymer that is either solid or in solution (between 0.5 and 5 g) is added to this solution of Fe(II) and Co(II) cations. Included among said natural biopolymer are natural polysaccharides, and more specifically alginates and chitosans. Thus, 1 g of chitosan and 625 μ l of acetic acid are
20 dissolved in a volume of 50 ml of a mixture of 75 mg of Fe(II) acetate and 75 mg of Co(II) acetate. A solution of sodium or ammonia alginate can also be prepared by dissolving 200 mg of commercial samples of these polysaccharides in 10 ml of distilled water.

- 25 The addition of the aqueous solution of the natural biopolymer to the solution of Fe and Co salts may cause immediate precipitation or the formation of a gel which may solidify, for example, by means of changes to pH. The addition can be carried out using needles, which may give rise to the formation of spherical precipitates. Thus, for example, gels derived from acidic solutions of chitosan
30 mixed with iron and cobalt salts can precipitate in the form of spheres by adding this solution dropwise with a syringe to a basic aqueous solution. In the case of alginate, the addition of aqueous solutions of this polysaccharide to the aqueous solution containing cationic iron and cobalt species causes instantaneous precipitation.

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The natural polysaccharide wet precipitate (hydrogel) containing the iron and cobalt species is dried by immersing the material in a series of six ethanol-water solutions at ratios of 10:90, 30:70, 50:50, 70:30, 90:10, 100:0, respectively. The dehydrated gel containing ethanol (alcogel) is finally dried by means of supercritical CO₂ to give an aerogel. Alternative drying methods give rise to materials with a low surface area, scarce porosity which subsequently after the pyrolysis lead to materials with a Fe-Co particle size greater than those which are obtained by the application of drying with supercritical CO₂ and do not promote the selective formation of isobutane.

The aerogel spheres of the polysaccharides containing Fe and Co salts are subjected to pyrolysis, avoiding the presence of oxygen in the process by means of a flow of an inert gas or gas under reduced pressure. N₂, Ar and H₂, inter alia, and mixtures of thereof in several ratios, can be used as inert gas. The flow must be regulated to assure that oxygen does not enter the in the oven. Alternatively, the pyrolysis chamber can be connected to a high vacuum system which maintains pressure less than 10⁻³ mm Hg. The temperature of the oven must be slowly increased and arrive at an ambient temperature between 800 and 1200 °C. A suitable temperature program can begin at room temperature at a speed of 1 °C /min until reaching a temperature of 200 °C which is maintained for 2 h and raised to 900 °C which is maintained for another 2 h. Next, the system is cooled at room temperature, maintaining at all times conditions preventing oxygen from entering. In general, heating must be carried out slowly and the maximum temperature must be within a range, lower temperatures do not cause graphitisation of the polysaccharide and temperatures higher than 1200 °C give rise to volatilisation of the carbon residue and the increase in average particle size.

The carbon residues containing iron and cobalt alloy nanoparticles which are obtained in pyrolysis can be ground before being used as a catalyst, or they can be subjected to ultrasounds or other treatments, such as mechanical agitation, so as to be dispersed in a liquid medium which can subsequently be eliminated by evaporation.

Characterisation

The materials the preparation of which has just been described in the preceding paragraphs predominantly consist of true Fe-Co alloy form nanoparticles embedded in a carbon matrix. The carbon corresponds to a turbostratic graphitic carbon which may sustain partial delamination or delamination at a high percentage to form sheets of defective graphene. The defects present in this graphenic carbon phase may consist of carbon vacancies, holes in the sheets, the presence of oxygenated groups and the possible presence of other heteroatoms, depending on the composition of the polysaccharide precursor. The residual oxygen content of these materials varies according to the pyrolysis conditions and the metal load being less than 20 %. Furthermore, when the precursor is chitosan the carbonaceous material contains a percentage of residual N at a value that may be 7 % by weight or lower. The pyrolysis of carrageenan may give rise to materials containing residual oxygen and the presence of a percentage of S less than 10 %. The presence of these heteroatoms can be determined and quantified by elemental analysis by combustion (N and S) and by means of x-ray photoelectron spectroscopy (XPS) analysis.

The metal content of these materials may vary in a wide range from very low values (0.05 % by weight), where the metal or metal alloys can be extremely dispersed, to 20 % by weight. The amount of metals can be determined by means of quantitative x-ray analysis or by means of elemental analysis by any inductively coupled plasma atomic emission or absorption technique. The accessibility of the metals in the carbon matrix is demonstrated by means of the treatment of these carbonaceous materials with hydrochloric acid, which produces leaching of a very high percentage of these metals which, in any event, is greater than 70 % and in many samples close to 90 %.

Under pyrolysis conditions, iron(II) and cobalt(II) ions and their species are reduced, preferably coming to form metallic Fe-Co alloy form nanoparticles. For samples with a high iron contained, the formation of low ratios of iron carbide, preferably Fe_5C_3 , has been observed. Significant amounts of cobalt carbides have not been observed. The predominant form of these metals is the true alloy form, two phases, fcc and bcc, being detected in several ratios. The values of

intermediate diffraction angles between the values corresponding to iron and cobalt indicate that they are alloys of these metals. The presence of these phases and the quantification of their ratios can be carried out for samples where the metal load is sufficient by means of the x-ray diffraction technique for powder samples.

Images of metallic nanoparticles by means of electron microscopy techniques reveal the morphology of the material. A particle size distribution histogram can be obtained by means of the dark field technique and by measuring the size of a statistically relevant number of these nanoparticles. These measurements have demonstrated that the pyrolysis conditions and the metal content affects the resulting nanoparticle size distribution. By means of the supercritical drying of CO₂ and slow heating in the pyrolysis process nanoparticles having a size around 5 nm can be obtained for metal content values greater than 10 % by weight.

High resolution images allow measuring the interplanar distance of these metallic nanoparticles which correspond with those to be expected for alloys of these metals.

If the Fe and Co content is very low, the particle size can be smaller, even obtaining very high dispersions of these metals in the matrix. Under certain circumstances, that dispersion can be considered a dispersion of atomic aggregates, or even of isolated atoms.

For purposes of illustrating the samples of the materials which can be prepared according to the present invention, Figures 2 to 8 show characterisation data for these samples.

Catalytic activity

The materials based on Fe-Co nanoparticles embedded in a carbon matrix have catalytic activity in the hydrogenation of CO₂. The reactions can be carried out in an SS-316 stainless steel reactor containing a fixed catalyst bed. The temperature of the reactor can be controlled with a thermocouple. The flow of gases is determined by means of mass flow control valves previously calibrated

with burettes. The gases introduced in the reactor can be preheated at the reaction temperature. Product analysis can be determined by means of a gas chromatograph connected to the reactor through an automatic injection valve. The chromatograph is coupled to a thermal conductivity detector and Ar is used as carrier gas. A separation column suitable is a PLOT Molsieve column which allows separating H₂, N₂, CO, CH₄, CO₂ and light hydrocarbons. The identity of the products can be confirmed by means of gas chromatography connected to a quadrupole mass detector. The possible formation of alcohols was quantified by means of a cold trap which condenses liquid compounds coming out of the reactor, analysing the condensed materials.

Control tests with an empty reactor in the absence of any catalyst or using as a catalyst defective graphenes not containing iron and/or cobalt indicate that the conversions of CO₂ in the range of temperatures between 300 and 550 °C is considerably less than that is achieved with the materials herein described. Moreover, the hydrogenation product formed under these conditions is predominantly methane, accompanied by significant amounts of CO (around 20 % in the system used), the presence of isobutane virtually not being observed under these conditions. Therefore, the formation of isobutane described in the present invention must be attributed to the action of the Fe and Co metal alloy in the form of nanoparticles dispersed on the carbon matrix.

Unexpectedly and without this result ensuing from the knowledge in the state of the art, some of the materials described in the present invention selectively produce the hydrogenation of CO₂ to isobutane, whereas other similar materials of the same composition but prepared without supercritical drying or with rapid heating programs give rise to the hydrogenation of CO₂ to methane. This latter behaviour is to be expected based on the state of the art, the selective formation of isobutane not being predictable based on the background described in the chemistry literature. For purposes of illustrating the results that may be obtained with the Fe-Co samples embedded in the carbon matrix, Tables 1-5 show some of the data obtained with these catalysts under the reaction conditions therein indicated.

Table 1. Codes and analytical data of some of the materials prepared according

to the present invention which have shown activity in the selective hydrogenation of CO₂, as indicated in Tables 2, 3 and 4.

Catalyst	Metal content (% by weight)	Fe/Co atomic ratio
Fe@(<i>N</i>)G	2.44	--
Fe_{0.46}Co_{0.54}@(<i>N</i>)G	9.25	Fe _{0.46} Co _{0.54}
Fe_{0.21}Co_{0.79}@(<i>N</i>)G	13.74	Fe _{0.29} Co _{0.71}
Co@(<i>N</i>)G	3.06	--

5 BRIEF DESCRIPTION OF THE FIGURES

Figure 1. Illustration of the preparation method for preparing the catalytic materials; i) Precipitation in a solution of 0.1 M NaOH; ii) H₂O/EtOH exchange; iii) Transformation of the alcogel into aerogel by means of drying with supercritical CO₂; iv) Pyrolysis of the aerogel in argon atmosphere.

Figure 2. Scanning electron microscopy images for the catalyst based on Fe-Co nanoparticles (atomic ratio of 1 to 3) in a total percentage by weight of 12.84 % embedded in a graphitic carbon matrix containing N as the dopant heteroatom (2.78 %) coming from chitosan as a precursor. Panel a shows a general view of the spheres obtained after drying with supercritical CO₂ and pyrolysis of a chitosan sample containing Fe and Co salts. Panels b and c show successive expansions of the walls of these spheres where the porosity of the material caused by gases being given off during pyrolysis can be seen. Image d is obtained in the dark field and Fe-Co alloy nanoparticles stand out as clear dots.

Figure 3. Transmission electron microscopy images taken for the catalyst based on Fe-Co nanoparticles (atomic ratio 1 of to 3) in a total percentage by weight of 12.84 % embedded in a graphitic carbon matrix containing N (2.78 %) as the dopant heteroatom after dispersing the solid in methanol with ultrasounds and deposited dropwise on the sample holder. Panels a and b show general images of the sample where the carbon matrix can be seen in clear contrast and the metallic nanoparticles as dark dots. Image c shows an expansion of one of these nanoparticles where the interplanar spacing which corresponds to an Fe and Co

alloy is indicated. The inserted image shows an electron diffraction of this nanoparticle indicating its crystallinity. Image d shows a dark-field image where the metallic nanoparticles stand out and the corresponding particle size distribution histogram with a modal distribution of between 5 and 10 nm.

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Figure 4. Raman spectra recorded at room temperature by 514 nm wavelength laser excitation of a sample such as that indicated in Figures 1, 2 and 3, fresh sample (black line) and after being used as a catalyst in a CO₂ hydrogenation cycle such as that corresponding to Table 1 (red line).

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Figure 5. Experimental x-ray diffractograms together with the adjustment obtained by the Rietveld method for a sample such as the one presented in Figures 2 and 3 before reaction (a) and after reaction following the cycle indicated in Table 2 (b) or after being subjected to thermal treatment at the temperature of 550 °C (c). The Rietveld analysis of the fresh sample presented in (a) indicates the presence of an Fe and Co alloy having two phases, fcc and bcc, at a ratio of 32 and 68, respectively. The samples after reaction (curve b) and after thermal treatment (curve c) also correspond to Fe-Co alloys, but show a decrease in the contribution of the fcc phase in favour of the bcc phase at a ratio, coinciding in both cases, of 12 to 88 %. The lower lines in the figure indicate the positions of the peaks expected according to the data available in crystallography databases for these Fe-Co alloys.

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Figure 6: Particle size distribution obtained in this example 2.

Figure 7: Histogram corresponding to the particle size distribution obtained in this example 3.

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Figure 8: Histogram corresponding to the particle size distribution obtained in example 4.

EXAMPLES

Having described the preparation of the samples and the selective catalytic activity to isobutane which corresponds to the present invention, it is additionally

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illustrated by means of the following examples.

Example 1. Preparation and catalytic activity of a sample based on Fe nanoparticles in a total percentage by weight of 2.44 % embedded in a graphitic carbon matrix containing N as the dopant heteroatom coming from chitosan as a precursor.

75 mg of iron(II) acetate are weighed and dissolved in 50 ml of distilled water. 1 g of chitosan and 625 μ l of acetic acid are added to this solution and it is magnetically stirred until the chitosan is completely dissolved. The resulting solution is added with a syringe provided with a needle 0.1 mm in internal diameter to 25 ml of an aqueous solution of NaOH (0.1 M). The addition causes the instantaneous precipitation of a greenish-white coloured solid collected by decantation. The spheres of this solid are dried by means of magnetic stirring for 10 min in 10 ml of a series of ethanol-water mixtures first having ratios of 10:90, then 30:70, next 50:50, 70:30, 90:10, and finally in pure ethanol. The spheres are separated by decantation and then dried by means of a drying apparatus with supercritical CO₂.

Once the spheres (400 mg) are dried, they are placed in a ceramic crucible with 10 ml capacity in the form of a thin layer and introduced in an electric oven with a volume of 350 ml. The oven is closed and an Ar current (200 ml $\times$ min⁻¹) is passed through same for 15 min. After this time has lapsed, the oven is heated at a speed of 1 °C $\times$ min⁻¹ to the temperature of 200 °C which is maintained for 2 h and subsequently to 900 °C, which is also maintained for a period of 2 h. The temperature inside the oven is determined with a thermocouple connected with the electric device that controls the heating. Finally, the oven is left to cool at room temperature, while the argon flow continues. The resulting carbonaceous sample is dispersed by treatment with ultrasounds (700 W) for 30 min in 20 ml of water. Lastly, the dispersed material is collected by lyophilising the suspension water. The resulting material corresponds to the sample indicated as Fe@(N)G in Table 1 and its catalytic activity is described in Tables 2, 3, and 4.

Example 2. Preparation and catalytic activity of a sample based on Fe-Co alloy nanoparticles at an atomic ratio of Fe_{0.46}Co_{0.54} in a total percentage by weight of

9.25 % embedded in a graphitic carbon matrix containing N as the dopant heteroatom coming from chitosan as a precursor.

The material of this example corresponds to the sample indicated as
5 $\text{Fe}_{0.46}\text{Co}_{0.54}@\text{(N)G}$ the analytical data of which is collected in Table 1 and the catalytic data of which is summarised in Tables 2, 3 and 4. This sample $\text{Fe}_{0.46}\text{Co}_{0.54}@\text{(N)G}$ was prepared following a method similar to the one described in example 1 with the difference that the first solution contains a mixture of 75 and 75 mg of iron(II) acetate and cobalt(II) acetate, respectively. This solution
10 containing the mixture of iron and cobalt salts was pooled with the acidic solution of chitosan in the amounts indicated in example 1, to proceed to precipitation thereof by changing the pH of the solution with NaOH in the same concentration and amounts indicated in example 1.

15 The resulting spheres were dehydrated by exchange with ethanol by suspension in the six ethanol-water or ethanol solutions indicated in example 1 before being before dried with supercritical CO_2 .

These chitosan spheres containing iron and cobalt are subjected to pyrolysis
20 under argon atmosphere in the conditions indicated in example 1 and are subsequently ground in an agate mortar until achieving the appearance of a fine powder. This fine powder without additives is introduced in the reactor to carry out the hydrogenation of CO_2 .

Figure 6 shows the particle size distribution obtained from dark-field transmission
25 electron microscopy images for the catalyst of this example 2.

Example 3. Preparation and catalytic activity of a sample based on Fe-Co alloy nanoparticles at an atomic ratio of $\text{Fe}_{0.29}\text{Co}_{0.71}$ in a total percentage by weight of 13.74 % embedded in a graphitic carbon matrix containing N as the dopant
30 heteroatom coming from chitosan as a precursor.

This material corresponds to the sample $\text{Fe}_{0.29}\text{Co}_{0.71}@\text{(N)G}$ the analytical data of which is indicated in Table 1 and the catalytic activity of which is summarised in Tables 2, 3 and 4. $\text{Fe}_{0.29}\text{Co}_{0.71}@\text{(N)G}$ was prepared following the method
35 indicated for the sample $\text{Fe}_{0.46}\text{Co}_{0.54}@\text{(N)G}$, but using the weights of iron(II)

acetate and cobalt (II) of 75 and 150 mg, respectively.

As can be seen in Tables 2, 3 and 4, this catalyst showed better isobutane selectivity data. Therefore, prolonged reaction tests of up to 500 h of reaction
5 under continuous flow were carried out under the reaction conditions indicated in Table 2. Catalyst deactivation was not observed, the material being stable for at least 500 h of continuous operation. Moreover, a sample of this material $\text{Fe}_{0.29}\text{Co}_{0.71}\text{@(N)G}$ after 30 h of reaction was characterised for the purpose of comparing its properties with those of the same fresh material. The resulting
10 spectra are shown in Figures 3 and 4 and are compatible with the catalytic stability observed for this material.

Figure 7 shows the histogram corresponding to the particle size obtained by dark-field transmission electron microscopy for the catalyst of this example 3.

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Example 4. Preparation and catalytic activity of a sample based on Co nanoparticles in a total percentage by weight of 3.06 % embedded in a graphitic carbon matrix containing N as the dopant heteroatom coming from chitosan as a precursor.

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The sample is referred to as Co@N(G) and was prepared following the method described in example 1, but replacing iron(II) acetate with cobalt(II) acetate at a weight of 75 mg, which was dissolved in a 50 ml volume of distilled water. The rest of the preparation method for preparing the spheres, the drying thereof by
25 means of exchange with ethanol and drying with supercritical CO_2 and pyrolysis thereof were carried out as indicated in example 1.

Figure 8 shows the particle diameter distribution histogram obtained by means of dark-field transmission electron microscopy images for the catalyst of example 4.

30

Example 5. Preparation and catalytic activity of a sample based on Fe-Co alloy nanoparticles at an atomic ratio of $\text{Fe}_{0.46}\text{Co}_{0.54}$ in a total percentage by weight of 9.25 % embedded in a graphitic carbon matrix containing N as the dopant heteroatom coming from chitosan as a precursor, but having a larger particle
35 size.

As indicated in preceding sections, the purpose of dehydration and supercritical drying, as well as the low pyrolysis speed, is to favour at all times interaction between the natural biopolymer and iron and cobalt salts, as well as the different materials that they generate in the course of pyrolysis. Dehydration without exchange with ethanol and supercritical drying gives rise to a low porosity in the biopolymer matrix, and the high pyrolysis speed determines that growth of the metallic Fe and Co alloy nanoparticles takes place in a less controlled manner. The result is a sample referred to as Fe_{0.46}Co_{0.54}@(N)G-Large, where the termination "Large" indicates that the average particle size of this sample is around 50 nm, much larger than that measured for sample Fe_{0.46}Co_{0.54}@(N)G and shown in Figure 3. When using this material Fe_{0.46}Co_{0.54}@(N)G-Large as a catalyst, it is observed that the product formed is methane with a selectivity of virtually 100 % (see Table 5).

Table 2a: Activity data for catalyst samples Fe@ (N)G; Fe_{0.46}Co_{0.54}@(N)G, Reaction conditions: Pressure (10 bar), flow rate (H₂: 3 ml/min, CO₂: 1 ml/min), weight of catalyst (20 mg).

	Fe@ (N)G							Fe _{0.46} Co _{0.54} @ (N)G							Fe _{0.46} Co _{0.54} @ (N)G- 2nd repetition														
T (°C)	C (%)	S (%) i-	S (%)	S (%)	S (%)	S (%) CH ₃ OH	S (%)	C (%)	S (%) i-	S (%)	S (%)	S (%)	S (%) CH ₃ OH	S (%)	C (%)	S (%) i-	S (%)	S (%)	S (%)	S (%) CH ₃ OH	S (%)	C (%)	S (%) i-	S (%)	S (%)	S (%)	S (%) CH ₃ OH	S (%)	
	CO ₂	C ₂ H ₆	CH ₄	CO	C ₂ H ₄		C ₂ H ₆	CO ₂	C ₂ H ₆	CH ₄	CO	C ₂ H ₄		C ₂ H ₆	CO ₂	C ₂ H ₆	CH ₄	CO	C ₂ H ₄		C ₂ H ₆	CO ₂	C ₂ H ₆	CH ₄	CO	C ₂ H ₄		C ₂ H ₆	
300	0.50	10.59	89.2	0.15	--*	--	0	16.93	74.49	24.37	0.55	0.47	0.12	0	11.30	27.95	70.60	0.51	0.75	0.19	0								0
350	3.10	6.79	92.93	0.28	--	--	0	28.10	74.62	22.28	0.43	2.36	0.31	0	27.11	33.41	61.98	1.32	2.47	0.32	0.50								0.50
400	11.62	1.58	98.24	0.18	--	--	0	46.02	61.79	31.13	1.09	4.38	0.44	1.18	47.41	49.56	41.19	2.40	4.14	0.41	2.29								
450	31.71	1.87	97.93	0.20	--	--	0	62.67	65.15	25.44	1.91	4.80	0.26	2.44	67.50	68.99	22.09	2.41	3.88	0.21	2.42								
500	51.55	3.01	96.79	0.20	--	--	0	76.30	79.96	16.61	1.03	1.89	0.03	0.47	79.45	83.36	13.72	1.04	1.57	0.03	0.29								
550	62.10	5.95	93.73	0.31	--	--	0	81.16	85.58	13.32	0.39	0.67	0	0.04	83.33	86.52	12.51	0.38	0.58	0	0.01								
600	51.73	3.08	96.71	0.20	--	--	0	79.96	83.13	13.83	0.95	1.66	0.02	0.40	79.26	84.10	13.10	0.97	1.45	0.01	0.36								
450	35.00	1.92	97.86	0.23	--	--	0	67.13	69.12	21.85	2.28	3.70	0.16	2.90	71.11	71.20	20.68	2.28	3.07	0.13	2.64								
400	14.72	1.13	98.65	0.22	--	--	0	49.96	50.99	39.40	2.34	3.67	0.31	3.29	53.93	52.15	38.88	2.37	3.13	0.27	3.20								
350	4.88	0.06	99.77	0.16	--	--	0	31.15	33.35	61.66	1.32	2.02	0.32	1.32	36.75	33.02	62.32	1.36	1.58	0.25	1.46								
300	1.25	0.25	99.75	0	--	--	0	12.95	23.63	75.07	0.47	0.64	0.20	0	17.07	21.08	77.26	0.53	0.46	0.14	0.52								

Table 2b: Activity data for catalyst samples $\text{Fe}_{0.29}\text{Co}_{0.71}@\text{(N)G}$ and $\text{Co}@\text{(N)G}$, Reaction conditions: Pressure (10 bar), flow rate (H_2 : 3 ml/min, CO_2 : 1 ml/min), weight of catalyst (20 mg).

	$\text{Fe}_{0.29}\text{Co}_{0.71}@\text{(N)G}$								$\text{Co}@\text{(N)G}$							
T (°C)	C (%)	S (%)	i-S (%)	S (%)	S (%)	S (%)	S (%)	S (%)	C (%)	S (%)	i-S (%)	S (%)	S (%)	S (%)	S (%)	S (%)
	CO_2	C_2H_{10}	CH_4	CO	C_2H_6	CH_3OH	C_2H_4		CO_2	C_2H_{10}	CH_4	CO	C_2H_6	CH_3OH	C_2H_4	
300	14.88	30.65	65.77	0.88	2.52	0.18	0		6.55	66.18	33.69	0.13	--	--	0	
350	32.61	50.01	44.66	2.17	1.51	0.11	1.53		18.03	60.61	39.24	0.16	--	--	0	
400	58.53	70.28	18.58	3.14	3.54	0.44	4.02		29.16	44.79	54.88	0.32	--	--	0	
450	77.12	84.17	9.05	1.97	3.03	0.21	1.57		53.74	66.58	31.43	1.32	--	--	0.67	
500	84.15	91.44	6.80	0.59	1.00	0.01	0.16		74.08	84.59	14.74	0.58	--	--	0.08	
550	87.16	92.50	6.85	0.26	0.35	0	0.04		80.01	86.86	12.90	0.24	--	--	0	
600	85.16	92.29	6.28	0.51	0.75	0.01	0.16		68.42	78.89	20.40	0.59	--	--	0.12	
450	79.41	86.91	7.31	1.64	2.60	0.08	1.46		46.94	58.62	39.53	1.07	--	--	0.78	
400	62.44	72.83	14.38	2.99	4.57	0.40	4.82		25.98	38.16	60.65	0.67	--	--	0.51	
350	36.34	51.91	37.64	2.44	3.51	0.68	3.83		11.75	28.15	71.57	0.28	--	--	0	
300	15.01	30.31	65.27	1.07	1.49	0.61	1.25		3.70	5.20	94.78	0.02	--	--	0	

5

Table 3: Influence of pressure on hydrogenation of the CO_2 catalysed by $\text{Fe}_{0.29}\text{Co}_{0.71}@\text{(N)G}$, Reaction conditions: Pressure (10 bar, 5 bar and atmospheric), flow rate (H_2 : 3 ml/min, CO_2 : 1 ml/min), weight of catalyst (20 mg)

	$\text{Fe}_{0.29}\text{Co}_{0.71}@\text{(N)G} - \text{P} = 10 \text{ bar}$						$\text{Fe}_{0.29}\text{Co}_{0.71}@\text{(N)G} - \text{P} = 5 \text{ bar}$						$\text{Fe}_{0.29}\text{Co}_{0.71}@\text{(N)G} - \text{atmospheric pressure}$					
T (°C)	C (%)	S (%)	S (%)	S (%)	S (%)		C (%)	S (%)	S (%)	S (%)	S (%)		C (%)	S (%)	S (%)	S (%)	S (%)	
	CO_2	i- C_4H_{10}	CH_4	CO	C_2H_6		CO_2	i- C_4H_{10}	CH_4	CO	C_2H_6		CO_2	i- C_4H_{10}	CH_4	CO	C_2H_6	
300	33.53	59.23	37.58	2.05	1.14		10.68	24.10	75.53	0.36	0		6.19	0	100	0	0	
350	68.16	81.15	13.09	2.73	3.02		28.02	29.09	69.65	0.95	0.30		16.81	3.14	96.45	0.41	0	
400	89.89	92.47	4.03	1.89	1.61		50.47	45.48	51.60	1.78	1.14		28.21	6.91	92.70	0.39	0	
450	96.73	97.47	1.67	0.65	0.22		70.58	63.09	33.90	1.90	1.12		51.19	23.84	75.96	0.20	0	
500	98.14	98.52	1.21	0.20	0.07		82.54	74.50	24.48	0.91	0.12		65.68	23.91	76.03	0.06	0	
550	98.98	98.83	0.99	0.12	0.07		88.26	77.83	21.90	0.27	0		73.07	21.04	78.94	0.02	0	

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Table 4a: Influence of the CO_2/H_2 ratio on hydrogenation of CO_2 catalysed by

Fe_{0.29}Co_{0.71}@(N)G, Reaction conditions: Pressure (10 bar), flow rate (H₂: 3 ml/min, CO₂: 1 ml/min), weight of catalyst (20 mg)

T (°C)	Fe _{0.29} Co _{0.71} @(N)G - CO ₂ :H ₂ = 1:1					Fe _{0.29} Co _{0.71} @(N)G - CO ₂ :H ₂ = 1:2				
	C (%)	S (%)	S (%)	S (%)	S (%)	C (%)	S (%)	S (%)	S (%)	S (%)
	CO ₂	i-C ₄ H ₁₀	CH ₄	CO	C ₃ H ₈	CO ₂	i-C ₄ H ₁₀	CH ₄	CO	C ₃ H ₈
300	8.81	24.58	74.22	1.20	0	16.02	44.98	52.87	1.61	0.53
350	17.05	34.29	62.30	2.06	1.34	30.52	57.52	37.33	2.57	2.59
400	27.66	52.45	39.92	3.25	4.38	47.23	69.71	22.43	3.34	4.51
450	42.73	70.03	23.93	2.85	3.19	66.04	83.87	11.65	2.35	2.13
500	52.94	79.53	19.47	0.81	0.20	75.19	90.61	8.64	0.63	0.12
550	56.66	78.66	21.16	0.19	0	77.93	90.28	9.56	0.16	0

5

Table 4b: Influence of the CO₂/H₂ ratio on hydrogenation of CO₂ catalysed by Fe_{0.29}Co_{0.71}@(N)G; Reaction conditions: Pressure (10 bar), flow rate (H₂: 3 ml/min, CO₂: 1 ml/min), weight of catalyst (20 mg)

T (°C)	Fe _{0.29} Co _{0.71} @(N)G - CO ₂ :H ₂ = 1:4					Fe _{0.29} Co _{0.71} @(N)G - CO ₂ :H ₂ = 1:7				
	C (%)	S (%)	S (%)	S (%)	S (%)	C (%)	S (%)	S (%)	S (%)	S (%)
	CO ₂	i-C ₄ H ₁₀	CH ₄	CO	C ₃ H ₈	CO ₂	i-C ₄ H ₁₀	CH ₄	CO	C ₃ H ₈
300	20.07	49.40	48.64	1.45	0.52	33.53	59.23	37.58	2.05	1.14
350	45.74	68.35	25.36	2.87	3.42	68.16	81.15	13.09	2.73	3.02
400	72.56	83.38	9.80	3.05	3.77	89.89	92.47	4.03	1.89	1.61
450	86.82	93.28	4.73	1.32	0.67	96.73	97.47	1.67	0.65	0.22
500	91.38	95.60	3.92	0.41	0.07	98.14	98.52	1.21	0.20	0.07
550	93.44	95.96	3.86	0.16	0.02	98.98	98.83	0.99	0.12	0.07

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Table 5: Catalytic activity data for a sample with a particle size greater than 50 nm corresponding to example 5.

T (°C)	C (%) CO ₂	S (%) CH ₄	S (%) C ₂ H ₆	S (%) C ₃ H ₈	S (%) C ₃ H ₆	S (%) CO
300	28.70	0	29.59	28.34	13.37	0.98

350	96.23	0	3.77	0	0	1.38
400	96.55	2.44	1.01	0	0	3.93
450	97.25	1.94	0.81	0	0	7.68
500	97.20	1.99	0.82	0	0	9.34

CLAIMS

1. A preparation method for preparing a catalyst based on iron nanoparticles, cobalt nanoparticles or alloys thereof embedded in a graphitic carbon matrix, characterised in that the preparation thereof comprises the following steps:
- a. forming a hydrogel by adding an aqueous solution of a natural biopolymer to a solution containing at least an Fe salt, a Co salt or mixtures of Fe and Co salts in a range of Fe/Co atomic ratios comprised between 0.1 and 1,
 - b. converting the hydrogel obtained in the preceding step into an alcogel by the gradual replacement of water with an alcohol which is selected from ethanol, methanol or propanol by suspending the hydrogel in a successive series of ethanol-water mixtures at ratios comprised between 10:90 and 100:0,
 - c. drying the alcogel resulting from the preceding step to obtain a dry aerogel mass by using supercritical CO₂,
 - d. pyrolysing the dry aerogel in the absence of oxygen in a range of temperatures between 800 and 1200 °C,
 - e. transforming the residues from pyrolysis into a material where the particle size of metallic oxide is comprised between 0.5 nm and 100 nm.
2. The preparation method for preparing a catalyst according to claim 1, wherein the biopolymer is a natural polysaccharide which is selected from chitosan, alginic acid, alkaline and alkaline earth metal alginates, carrageenan and mixtures at any ratio of any combination thereof.
3. The preparation method for preparing a catalyst according to claims 1 or 2, wherein the ratio between the natural biopolymer and the Fe salt, Co salt or mixture of Fe and Co salts is comprised between 100 and 100,000.
4. The preparation method for preparing a catalyst according to any one of claims 1 to 3, wherein the Fe or Co salt is selected from Fe or Co acetate, nitrate or salt complexes with ammonia.

5. The preparation method for preparing a catalyst according to any one of claims 1 to 4, wherein pyrolysis in the absence of oxygen is performed under vacuum conditions at a pressure of less than 10^{-3} mm Hg.

5

6. The preparation method for preparing a catalyst according to any one of claims 1 to 4, wherein pyrolysis in the absence of oxygen is performed in the presence of a flow of an inert gas which is selected from N₂, Ar, He or mixtures thereof.

10

7. The preparation method for preparing a catalyst according to any one of claims 1 to 6, wherein pyrolysis is programmed at an initial speed of 1 °C/min until reaching 200 °C, which is maintained for 2 h and subsequently raised to 900 °C which is maintained for 2 h, followed by cooling with the absence of oxygen being maintained.

15

8. The preparation method for preparing a catalyst according to any one of claims 1 to 7, wherein the transformation of the residue from pyrolysis is carried out by means of a method which is selected from grinding, treatment with ultrasounds or mechanical agitation so as to be dispersed in a liquid medium which is subsequently eliminated by evaporation.

20

9. The preparation method for preparing a catalyst according to any of claims 1 to 8, wherein the transformation of the residues from pyrolysis into a material in which the particle size of metallic oxide is comprised between 2 nm and 20 nm.

25

10. A catalyst prepared by means of a method according to claims 1 to 9, characterised in that:

30

- the residual oxygen content is less than 20 %,
- the Fe and/or Co content is comprised between 0.05 % and 20 % by weight,
- it is in the form of metallic oxide nanoparticles having sizes comprised between 0.5 and 100 nm embedded in a graphitic carbon matrix.

35 11. The catalyst according to claim 10, wherein the carbon matrix contains a

percentage of N equal to or less than 7 % when the biopolymer is chitosan.

12. The catalyst according to claim 11, wherein the carbon matrix contains a percentage of S less than 10 % when the biopolymer is carrageenan.

5

13. The catalyst according to any of claims 10 to 12, wherein the metallic oxide nanoparticles have a size of between 2 nm and 20 nm and are embedded in a graphitic carbon matrix.

10 14. Use of a catalyst according to claims 10 to 13 for the selective hydrogenation of carbon dioxide to isobutane.

15 15. The use of a catalyst according to claim 14, wherein the temperature of the carbon dioxide hydrogenation reaction is comprised between 350 °C and 600 °C.

16. The use of a catalyst according to claims 14 or 15, wherein the molar ratio between CO₂ and H₂ is comprised between 1/2 and 1/7.

20 17. The use of a catalyst according to any one of claims 14 to 16, wherein the carbon dioxide hydrogenation reaction takes place at a pressure comprised between 100 and 2000 KPa.

FIG. 1

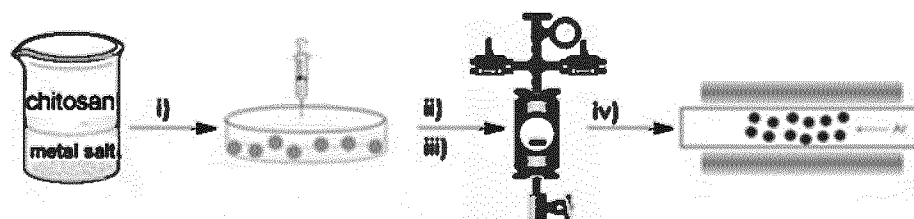


FIG. 2

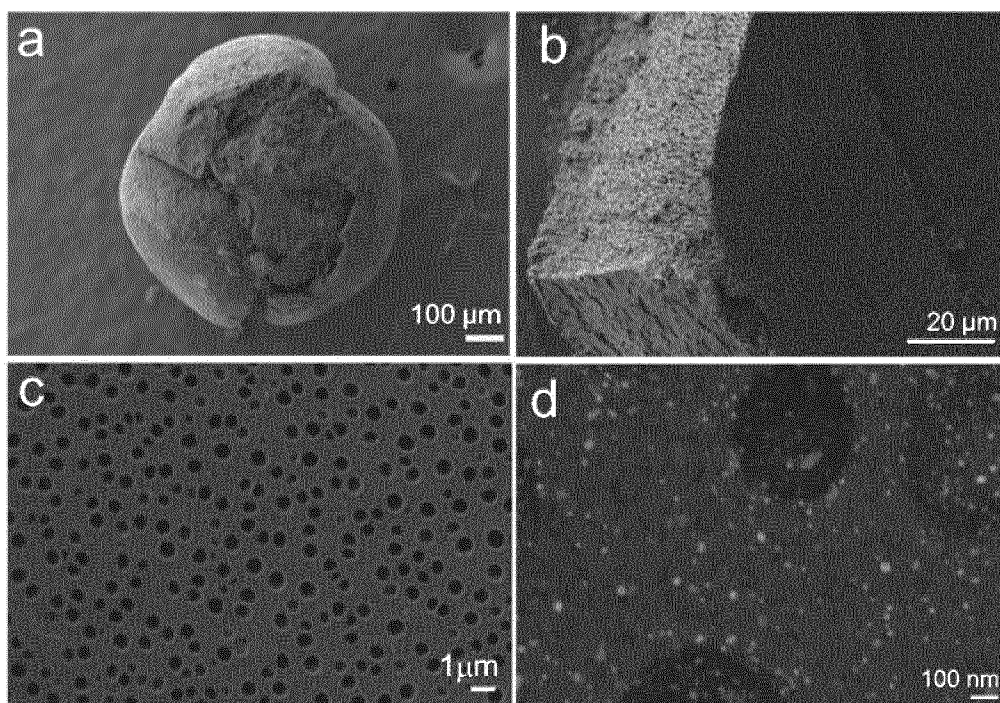


FIG. 3

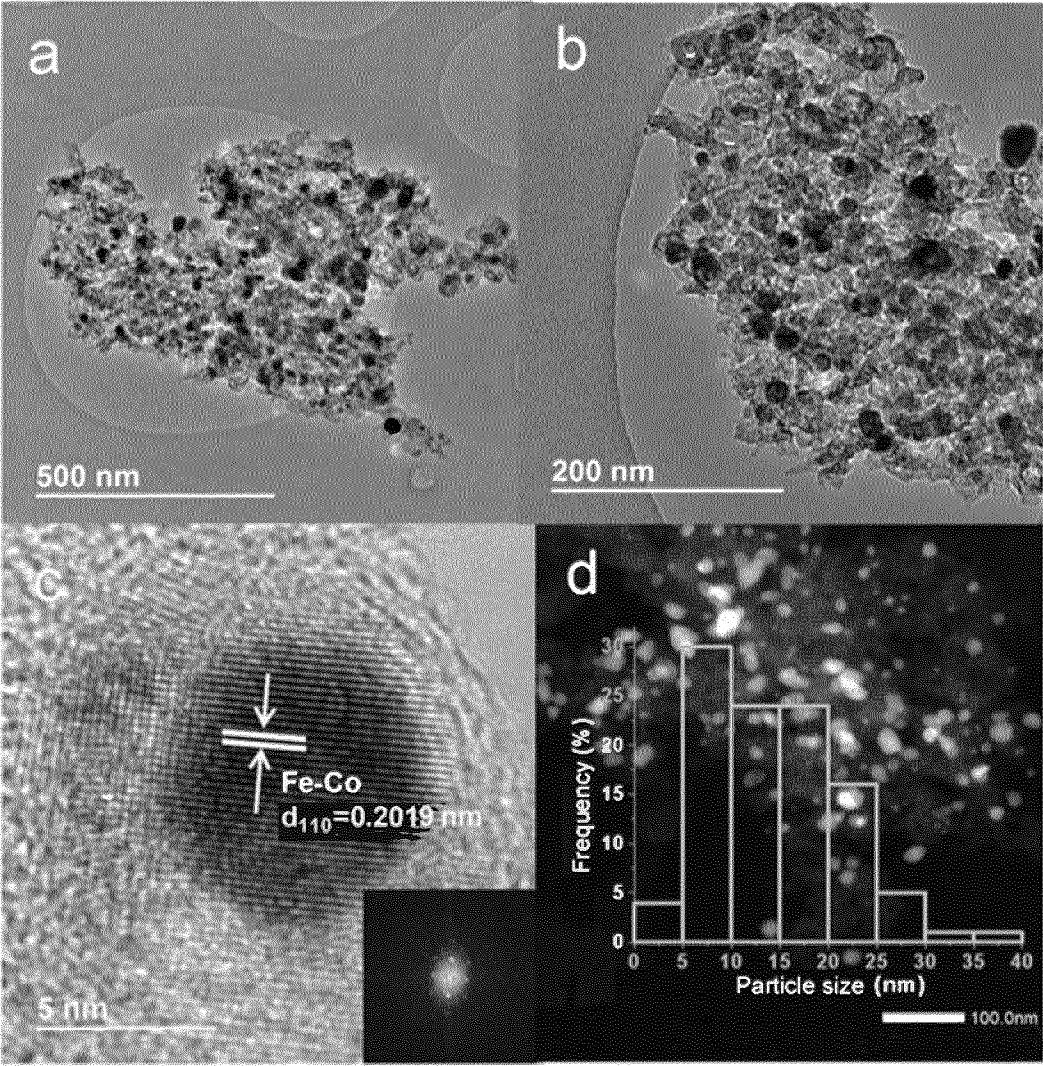


FIG. 4

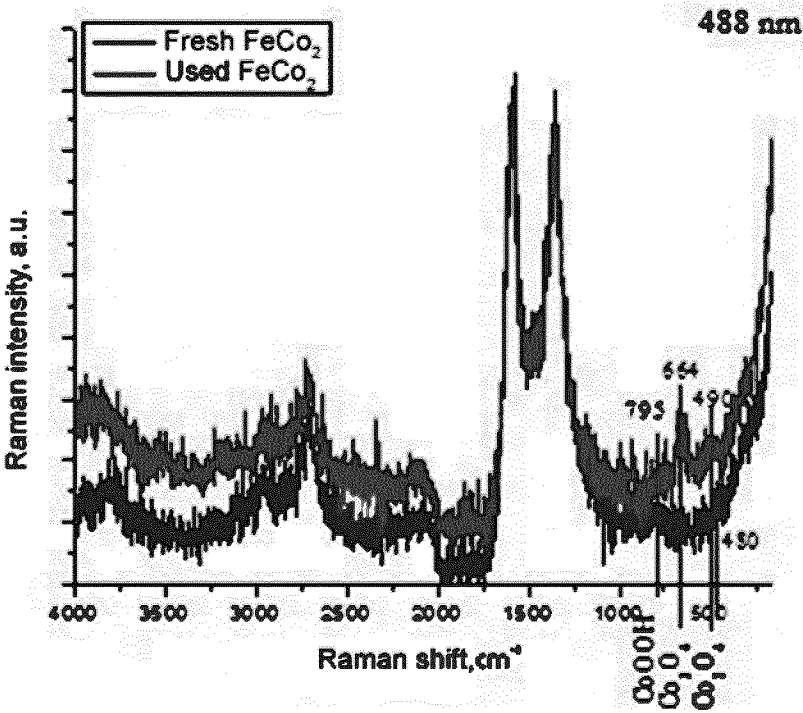


FIG. 5

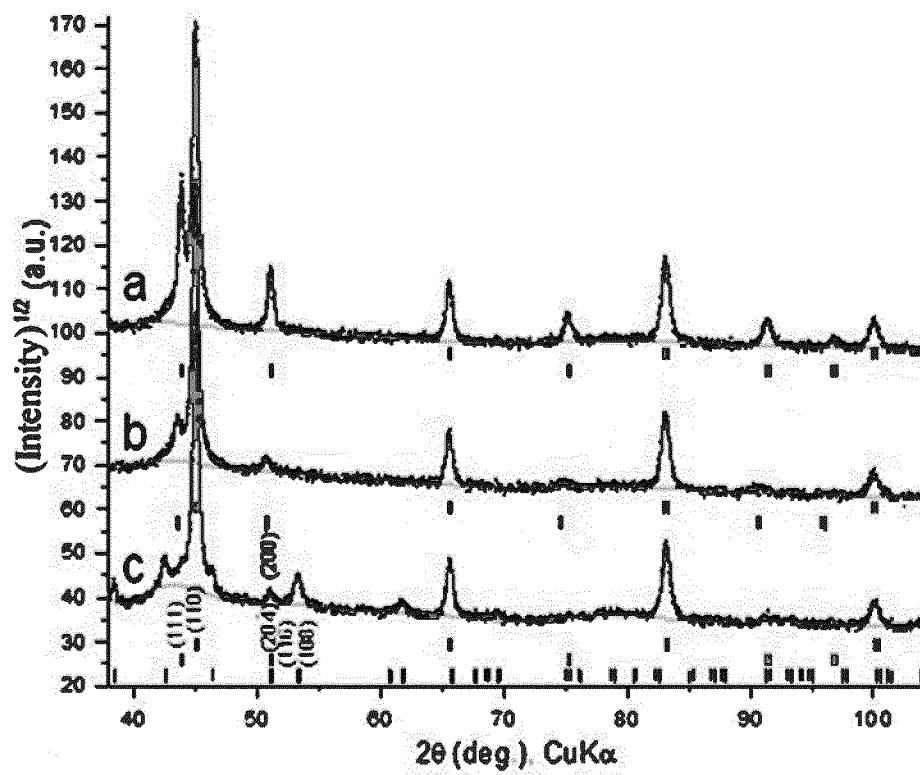
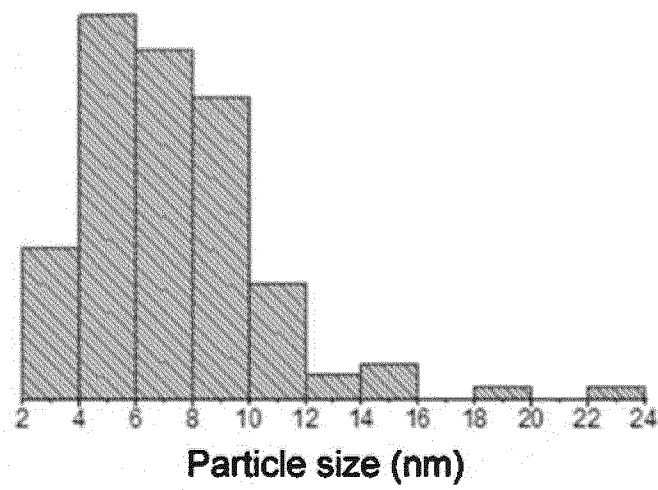


FIG. 6



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FIG. 7

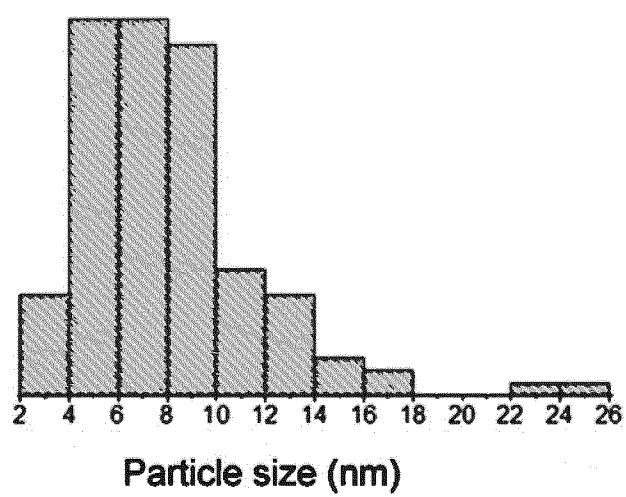
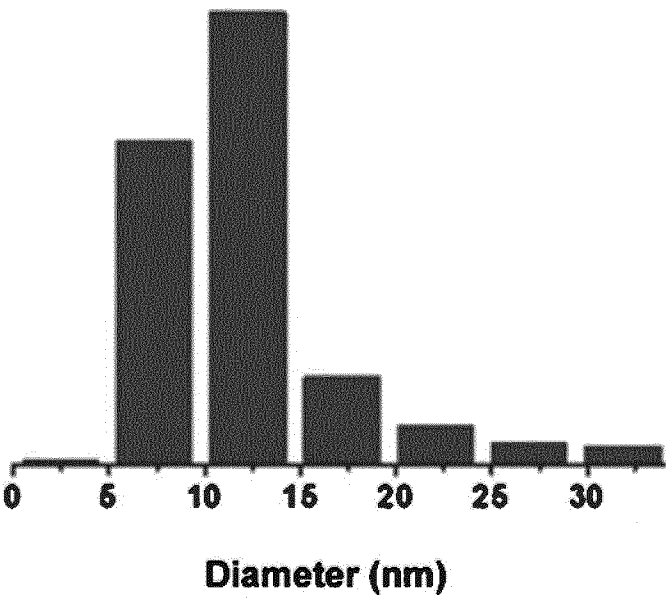


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/082589

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J23/75 B01J21/18 B01J37/16 B01J37/02 B01J35/00
B01J37/08 B01J37/03 C07C1/12

ADD.

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)

B01J C07C H01M

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 practicable, 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	FENG JIANG ET AL: "Hydrogenation of CO₂ into hydrocarbons: enhanced catalytic activity over Fe-based Fischer-Tropsch catalysts", CATALYSIS SCIENCE & TECHNOLOGY, vol. 8, no. 16, 1 January 2018 (2018-01-01), pages 4097-4107, XP055673376, ISSN: 2044-4753, DOI: 10.1039/C8CY00850G page 4098, right-hand column, last paragraph - page 4099, left-hand column, paragraph 2; figure 2d; table 2 page 4099, left-hand column, paragraph 2.3 - page 4099, right-hand column, paragraph 1 ----- -/-	10-17

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

5 March 2020

Date of mailing of the international search report

16/03/2020

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Beckmann, Oliver

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/082589

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	A A VASILEV ET AL: "Morphology and dispersion of FeCo alloy nanoparticles dispersed in a matrix of IR pyrolyzed polyvinyl alcohol", I O P CONFERENCE SERIES: MATERIALS SCIENCE AND ENGINEERING, vol. 347, 1 April 2018 (2018-04-01), page 012011, XP055673433, GB ISSN: 1757-8981, DOI: 10.1088/1757-899X/347/1/012011 page 1, paragraph 1 - paragraph 2 page 4, paragraph 2; figure 6 -----	10-17
Y	DATABASE WPI Week 201501 Thomson Scientific, London, GB; AN 2014-W59843 XP002798110, -& CN 104 057 080 B (BEIJING INST TECHNOLOGY) 22 June 2016 (2016-06-22) abstract; example 4 -----	1-9
Y	HORGA ET AL: "Iontropic alginate aerogels as precursors of dispersed oxide phases", APPLIED CATALYSIS A: GENERAL, ELSEVIER, AMSTERDAM, NL, vol. 325, no. 2, 22 May 2007 (2007-05-22), pages 251-255, XP022088385, ISSN: 0926-860X, DOI: 10.1016/J.APCATA.2007.02.042 page 252, left-hand column, paragraph 2. Experimental - right-hand column, paragraph 2 -----	1-9
Y	TSIOPTSIAS C ET AL: "Chitin and carbon aerogels from chitin alcogels", CARBOHYDRATE POLYMERS, APPLIED SCIENCE PUBLISHERS, LTD. BARKING, GB, vol. 76, no. 4, 16 May 2009 (2009-05-16), pages 535-540, XP026061212, ISSN: 0144-8617, DOI: 10.1016/J.CARBPOL.2008.11.018 [retrieved on 2008-11-21] page 536, left-hand column, paragraph 2.2 Preparation and characterisation - right-hand column, paragraph 3 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/082589

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 104057080	B	22-06-2016	NONE
