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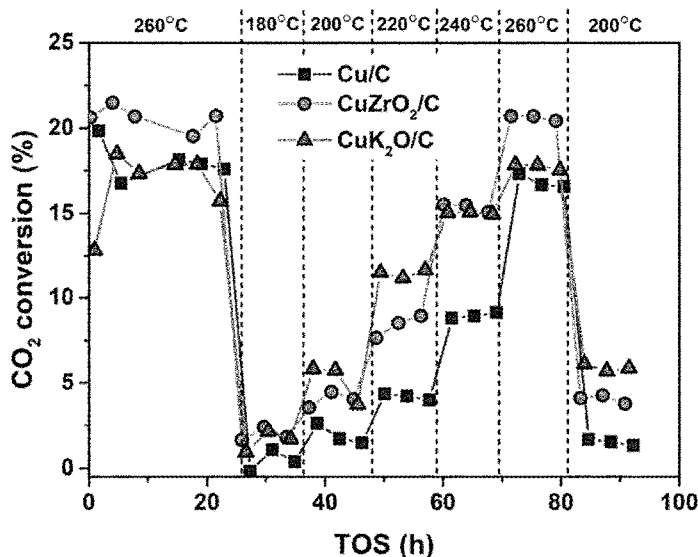
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Fig. 1

(57) **Abstract:** Subject of the invention is a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$.

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METAL CATALYSTS FOR A HYDROGENATION OF CO₂ INTO CO

Field of the invention

- 5 The invention relates to metal catalysts for a hydrogenation of carbon dioxide (CO₂) into carbon monoxide (CO) and to related methods and uses.

Background of the invention

- 10 Synthesis gas, a mixture of carbon monoxide and hydrogen (H₂), is a crucial intermediate in many important chemical processes such as methanol synthesis and Fischer-Tropsch synthesis. The production of synthesis gas in a sustainable manner has been the subject of much research revolving around the exploitation of alternative feed stocks.
- 15 The thermocatalytic conversion of carbon dioxide into carbon monoxide has been known since long as the reverse water-gas shift (rWGS) reaction, which could play a major role in carbon dioxide upgrading in view of the common use of CO and synthesis gas in industry. The rWGS reaction refers to the catalytic conversion of CO₂ to CO under a reducing atmosphere, which consumes one unit of CO₂ and H₂ per unit of CO and water (H₂O)
- 20 produced. The reaction competes with methane production and the forward water gas shift reaction from CO to CO₂. The rWGS reaction is endothermic, with CO formation favoured at high temperature (> 700°C). The reaction stoichiometry and energetics are shown below:



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- For rWGS reactions at higher temperatures, various catalysts have been tested over time. For example, US 2018/0093888 A1 describes a method of preparing syngas in a reaction chamber which can include a solid-supported catalyst which itself can include in particular copper (Cu) and manganese (Mn). Lower-temperature rWGS operation could improve the
- 30 energy efficiency thereof, but the development of efficient catalysts for a low temperature rWGS (e.g., <600°C) is a great challenge, especially when aiming at maximum CO yield at minimum CH₄ selectivity. According to US 2011/0105630 A1, the rWGS reaction can

take place at modest temperatures over promoted ceria, and a couple of ceria-based catalysts are described in this context. Also with an aim to achieve a suitable rWGS operation at lower temperatures, certain copper-zinc(Zn)-based catalysts have been tested in CN 103230799 A1. The catalyst generally described therein has the structural formula $\text{Cu}_a\text{Zn}_b\text{M}_c$, wherein M is selected from one or more of transition metal elements, 5 alkali metals, alkaline-earth metals or rare earth metals.

For a combination of a rWGS reaction and a Fischer-Tropsch reaction, US 2021/0230005 A1 mentions iron-based materials as potential catalysts. However, it is suggested to perform the rWGS reaction at a rather high temperature of 300° C to 475°C. 10 Further, for the iron-based materials, FeCuKAl is mentioned as an example. However, it is not stated whether the metal species in this catalyst are present in metallic form or in oxidic form, and there is no specific synthesis example in which a carbon support would have been used. Additionally, the only specifically synthesized catalyst is of the formula 15 $100\text{Fe}-13\text{Cu}-12\text{Al}-15\text{K}$ (in weight percent based on the mass of the element) and thus contains, in terms of atoms or molar content, significantly more potassium (having a standard atomic weight of 39.10) than copper (having a standard atomic weight of 63.54). Moreover, this catalyst is used in US 2021/0230005 A1 as a Fischer-Tropsch synthesis catalyst and not as an rWGS catalyst, for which rather platinum on a ceria support is suggested. Accordingly, no performances of the iron-based catalyst in an rWGS reaction 20 are reported in US 2021/0230005 A1, especially not at lower temperatures.

In WO 2014/116341 A1 supported copper catalysts are used in a different technical context, namely for preparing trihalosilanes. As second metal species of these catalysts apart from copper either gold or magnesium are employed. In US 8,785,343 B2, a supported copper-based catalyst is described which additionally contains potassium in a comparably high amount ($\text{Cu}:\text{K} = 6.5:1$) and is used for a conversion of isobutane to isobutene. US 2023/0150823 A1 describes various catalysts for a CO_2 hydrogenation to CO. In one case, a copper catalyst containing a fairly high amount of potassium 30 ($\text{Cu}:\text{K} = 2.9:1$) supported on SiO_2 is used.

It remains highly desired to develop new catalytic materials that achieve high CO yields in CO_2 hydrogenation at low temperatures with a view to stability and energy efficiency. At the same time, an improved catalyst should combine a maximum CO productivity with a

negligible selectivity to methane which, according to thermodynamics, is formed more favourably at lower temperatures but is an undesired by-product. A respective catalyst should yield no by-products or only by-products which allow for an easy purification of the product mixture. Overall, there remains a general desire for improved catalysts for a hydrogenation of CO₂ into CO.

Problem underlying the invention

It is an object of the present invention to provide a catalyst for a hydrogenation of CO₂ into CO which at least partly overcomes the drawbacks encountered in the art.

It is in particular an object of the present invention to provide a catalyst for a hydrogenation of CO₂ into CO which leads to an improved CO yield and/or an improved selectivity for CO.

It is furthermore an object of the present invention to provide a catalyst for a hydrogenation of CO₂ into CO which allows to perform the hydrogenation at lower temperatures and/or has a higher thermal stability.

It is additionally an object of the present invention to provide a catalyst for a hydrogenation of CO₂ into CO which can reduce undesired formation of methane and/or leads to a product which can be purified more easily.

It is also an object of the present invention to provide a method of producing carbon monoxide as well as a use of a catalyst for catalysing a hydrogenation of CO₂ into CO which at least partly overcome the drawbacks encountered in the art.

Disclosure of the invention

Surprisingly, it has been found that the problem underlying the invention is overcome by catalysts, methods and uses (as technical means) according to the claims. Further embodiments of the invention are outlined throughout the description.

Subject of the invention is a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$. As used herein, the expression “excluding magnesium” means that the promotor metal is not magnesium (Mg). In other words, a catalyst comprising a copper-promotor metal phase supported on carbon according to the present invention does not contain magnesium. The copper (Cu) of the copper-promotor metal phase is the only copper comprised by the catalyst, and the alkali metal or alkaline earth metal of the copper-promotor metal phase is the only alkali metal or alkaline earth metal comprised by the catalyst. The atomic ratio between copper and promotor metal may also be referred to as Cu:promotor metal ratio, and this ratio is equal to or larger than 7:1 (i.e., $\geq 7:1$). In other words, the catalyst according to the present invention comprises, on average, seven or more copper atoms per comprised promotor metal atom (or promotor metal ion, as the alkali metal or alkaline earth metal is preferably present in an oxidation state of > 0). This can alternatively be defined by a concentration of Cu in the catalyst which is seven or more times higher than the concentration of promotor metal in the catalyst, wherein the concentrations can especially be given in mol%. Hence, the ratio between copper and promotor metal can also be defined as $\text{mol\%}(\text{Cu}) \geq 7 \cdot \text{mol\%}(\text{promotor metal})$, based on the total atomic composition of the catalyst. It can thus also be said that the copper in the copper-promotor metal phase is doped with the promotor metal. The doping with the alkali metal or alkaline earth metal leads to the achieved effects explained herein, i.e., they promote the catalytic activity of the copper. Therefore, the alkali metal and alkaline earth metal, respectively, are herein commonly referred to as “promotor metal”.

As used herein, the term “alkali metal” is used in the usual chemical sense and represents the group of elements consisting of lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr). As used herein, the term “alkaline earth metal” is basically used in the usual chemical sense and represents the group of elements consisting of beryllium (Be), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra), but excludes magnesium (Mg). As used herein, the term “alkaline earth metal” does therefore not encompass magnesium. As used herein, the term “metal” does not require the metal element to be present in metallic form, i.e., to be present in an oxidation state of $= 0$. Rather, the metal element can well be present in a different oxidation state and

especially in an oxidation state of > 0 . For example, it is preferred that the promotor metal, i.e., the alkali metal or the alkaline earth metal, is present in the form of an oxide (e.g., as Na_2O , K_2O , CaO or SrO). It is also contemplated that the promotor metal may preferably be present in the form of a salt, especially in the form of a carbonate, a nitrate, or an acetate.

The carbon (C) comprised by the catalyst according to the present invention acts as a support for the copper-promotor metal phase and may thus also be referred to as carbon support, or carbonaceous support. The copper and the promotor metal are deposited on this carbon. It can thus also be said that the catalyst according to the present invention comprises a carbon-supported copper-promotor metal phase. Optionally, the catalyst according to the present invention contains the copper and the promotor metal as the only metal species (metal elements). In an example, the catalyst according to the present invention is composed of the copper, the promotor metal, the carbon and optionally oxygen, especially oxygen which together with the promotor metal forms a corresponding promotor metal oxide.

The catalyst according to the present invention is able to achieve the CO_2 conversion limit (the energy threshold at which CO_2 is converted with H_2 into CO and H_2O) at low temperatures while exhibiting improved CO yield (and hence improved CO_2 conversion) and a nearly 100% selectivity to CO . Accordingly, the catalyst allows for an improved hydrogenation of CO_2 into CO at lower temperatures. The catalyst according to the present invention further exhibits a higher thermal stability at comparably higher temperatures. Moreover, when using the catalyst according to the present invention for the hydrogenation of CO_2 into CO , methanol instead of methane is typically detected as the only by-product which facilitates product purification afterwards. In other words, when using the catalyst according to the present invention, the formation of methanol as the only by-product is favoured which advantageously contributes to an easier purification of the product of the CO_2 hydrogenation reaction.

Without wishing to be bound to theory, it is assumed that the copper comprised by the catalyst ensures a selective conversion of CO_2 to CO , whereas the promotion by the promotor metal (the comprised alkali metal or alkaline earth metal) improves the performance in many ways and in particular leads to higher thermal stability, facilitates

CO₂ activation, and/or suppresses methane formation. In this context, it has been surprisingly found that these effects can be simultaneously improved when a reduced amount of promotor metal is present in the copper-promotor metal phase of the catalyst according to the present invention. That is, the mentioned effects can be simultaneously improved when significantly less promotor metal than copper is present as indicated by the atomic ratio between copper and promotor metal of $\geq 7:1$, which means that the copper is doped with, or promoted by, the promotor metal.

In this context, it is particularly preferred for a catalyst according to the present invention that the atomic ratio between copper and promotor metal ranges from $\geq 7:1$ to $\leq 30:1$, more preferably from $\geq 7:1$ to $\leq 20:1$, yet more preferably from $\geq 7:1$ to $\leq 15:1$, still more preferably from $\geq 7:1$ to $\leq 13:1$ and even more preferably from $\geq 9:1$ to $\leq 11:1$. It is most preferred that the atomic ratio between copper and promotor metal is 10:1. With the mentioned atomic ratios, the CO yield and the selectivity to CO in a hydrogenation of CO₂ into CO can be continuously further improved. Additionally, with the mentioned atomic ratios, the catalyst becomes more and more thermally stable, and the formation of by-products and especially of methanol is more and more suppressed so that the purification of the product of the hydrogenation is further simplified. On the other hand, handling difficulties potentially associated with the incorporation of very tiny amounts of promotor metal are avoided, without jeopardizing the afore-mentioned effects. These preferred atomic ratios can thus achieve a particularly suitable balance between advantageous effects in a CO₂ hydrogenation using the catalyst, and easy handling of raw materials for synthesizing the catalyst.

It is preferred for a catalyst according to the present invention that the copper is present in an amount of 1 to 50 wt.%, more preferably in an amount of 4 to 20 wt.%, still more preferably in an amount of 6 to 12 wt.%, and even more preferably in an amount of 8 to 10 wt.%, respectively based on the total weight of the catalyst. It is most preferred that the copper is present in an amount of 9 wt.%, based on the total weight of the catalyst. With such amounts of copper, the selectivity of the conversion of CO₂ to CO can be continuously further improved. For these preferred copper loadings, it is particularly preferred that the carbon is made from layered graphene sheets, more preferred from GNP500 as detailed herein.

It is preferred for a catalyst according to the present invention that the promotor metal is sodium, potassium, or a mixture thereof. The presence of sodium and/or potassium in the catalyst leads to a particular promotion of the rWGS catalytic characteristics of the catalyst, especially in terms of higher thermal stability, easier CO₂ activation, and suppression of methane formation.

It is preferred for a catalyst according to the present invention that the promotor metal is sodium which is present in an amount of 0.05 to 0.60 wt.%, more preferably in an amount of 0.10 to 0.50 wt.%, still more preferably in an amount of 0.15 to 0.45 wt.%, and even more preferably in an amount of 0.20 to 0.40 wt.%, respectively based on the total weight of the catalyst. It is most preferred that the promotor metal is sodium which is present in an amount of 0.30 wt.%. When the promotor metal is sodium which is present in such amounts, this particularly further improves thermal stability, CO₂ activation, and suppression of methane formation. For all these preferred sodium loadings, it is particularly preferred that the carbon is made from layered graphene sheets, more preferred from GNP500 as detailed herein.

It is preferred for a catalyst according to the present invention that the copper is present in an amount of 1 to 50 wt.% and that the promotor metal is sodium which is present in an amount of 0.05 to 0.60 wt.%, more preferred that the copper is present in an amount of 4 to 20 wt.% and that the promotor metal is sodium which is present in an amount of 0.10 to 0.50 wt.%, still more preferred that the copper is present in an amount of 6 to 12 wt.% and that the promotor metal is sodium which is present in an amount of 0.15 to 0.55 wt.%, and even more preferred that the copper is present in an amount of 8 to 10 wt.% and that the promotor metal is sodium which is present in an amount of 0.20 to 0.40 wt.%, respectively based on the total weight of the catalyst, in order to simultaneously achieve the above-described effects of the preferred copper loadings and the preferred sodium loadings. In this respect, it is most preferred that the copper is present in an amount of 9 wt.% and that the promotor metal is sodium which is present in an amount of 0.30 wt.%. For all these preferred combinations of copper loadings and sodium loadings, it is particularly preferred that the carbon is made from layered graphene sheets, more preferred from GNP500 as detailed herein.

It is preferred for the catalyst according to the present invention that the promotor metal is potassium which is present in an amount of 0.20 to 1.00 wt.%, more preferably in an amount of 0.30 to 0.90 wt.%, still more preferably in an amount of 0.40 to 0.80 wt.%, and even more preferably in an amount of 0.50 to 0.70 wt.%, respectively based on the total weight of the catalyst. It is most preferred that the promotor metal is potassium which is present in an amount of 0.60 wt.%. When the promotor metal is potassium which is present in such amounts, this particularly further improves thermal stability, CO₂ activation, and suppression of methane formation. For all these preferred potassium loadings, it is particularly preferred that the carbon is made from layered graphene sheets, more preferred from GNP500 as detailed herein.

It is preferred for a catalyst according to the present invention that the copper is present in an amount of 1 to 50 wt.% and that the promotor metal is potassium which is present in an amount of 0.20 to 1.00 wt.%, more preferred that the copper is present in an amount of 4 to 20 wt.% and that the promotor metal is potassium which is present in an amount of 0.30 to 0.90 wt.%, still more preferred that the copper is present in an amount of 6 to 12 wt.% and that the promotor metal is potassium which is present in an amount of 0.40 to 0.80 wt.%, and even more preferred that the copper is present in an amount of 8 to 10 wt.% and that the promotor metal is potassium which is present in an amount of 0.50 to 0.70 wt.%, respectively based on the total weight of the catalyst, in order to simultaneously achieve the above-described effects of the preferred copper loadings and the preferred potassium loadings. In this respect, it is most preferred that the copper is present in an amount of 9 wt.% and that the promotor metal is potassium which is present in an amount of 0.60 wt.%. For all these preferred combinations of copper loadings and potassium loadings, it is particularly preferred that the carbon is made from layered graphene sheets, more preferred from GNP500 as detailed herein.

It is preferred for a catalyst according to the present invention that the promotor metal is calcium, strontium, or a combination thereof. When the promotor metal is calcium, strontium or a combination thereof an improved CO₂ conversion as well as an improved selectivity to CO are achievable already at low temperatures. Especially, when a hydrogenation of H₂ is performed at a temperature of 260°C or less, CO₂ conversion and CO selectivity are particularly improved when the promotor metal in the catalyst according to the present invention is selected from calcium, strontium, and combinations thereof.

It is preferred for the catalyst according to the present invention that the carbon is selected from layered graphene sheets, carbon nanofibers, carbon nanotubes, graphite and activated carbon, and is most preferably made of layered graphene sheets. Such a carbon as support for the copper-promotor metal phase leads to a further improved CO₂ conversion and consequently to a further enhanced CO yield. Simultaneously, by such a carbon as support for the copper-promotor metal phase, the selectivity for CO in a hydrogenation reaction converting CO₂ into CO is further increased.

Additionally, layered graphene sheets (sometimes also referred to as graphene nanoplatelets, wherein stacked sheets ultimately form a graphitic material), or some other sort of at least partially ordered graphitic material, which together with the layered graphene sheets may commonly referred to as an at least partially crystalline carbon material, as support can further promote the distribution of the copper and the promotor metal on the support which can further enhance the hydrogenation characteristics and in particular the CO yield and CO selectivity. Additionally, using at least partially crystalline carbon material for the support can help to make the catalyst mechanically, chemically and/or thermally robust enough. For example, at higher temperatures an undesired methanation of the carbon support may occur. When using an at least partially crystalline carbon material for the support, such an undesired methanation can be reduced. In this context, it is preferred that the at least partially crystalline carbon material for the support has a Brunauer–Emmett–Teller (BET) surface area of $> 50 \text{ m}^2/\text{g}$, more preferably of $> 100 \text{ m}^2/\text{g}$, still more preferably of $> 200 \text{ m}^2/\text{g}$. In a particularly preferred case, the at least partially crystalline carbon material for the support has a BET surface area of 300 to $700 \text{ m}^2 \text{ g}^{-1}$, more preferably of 400 to $600 \text{ m}^2 \text{ g}^{-1}$ and still more preferably of 450 to $550 \text{ m}^2 \text{ g}^{-1}$. With the above-mentioned BET surface areas the deposition of copper and promotor metal can be promoted which leads to further improved rWGS characteristics. It is also preferred that the layered graphene sheets have a total pore volume of 0.70 to $1.10 \text{ cm}^3 \text{ g}^{-1}$, more preferably of 0.80 to $1.00 \text{ cm}^3 \text{ g}^{-1}$ and still more preferably of 0.85 to $0.95 \text{ cm}^3 \text{ g}^{-1}$. With such a total pore volume the deposition of copper and alkali metal can be promoted which leads to further improved rWGS characteristics. It is most preferred that graphene nanoplates commercially available under the trade name GNP500 (herein sometimes also just named “GNP”; having a BET surface area of $496 \text{ m}^2 \text{ g}^{-1}$ and a total

pore volume of $0.91 \text{ cm}^3 \text{ g}^{-1}$) are used as the carbon of the catalyst according to the present invention.

It is preferred for a catalyst according to the present invention that the catalyst has a grain size of 10 to $300 \mu\text{m}$, more preferably of 25 to $250 \mu\text{m}$, still more preferably of 50 to $200 \mu\text{m}$, and even more preferably of 75 to $150 \mu\text{m}$. With such grain sizes, the catalyst may be used in already existing equipment while simultaneously enhancing the CO yield in a hydrogenation of CO_2 into CO.

It is preferred for a catalyst according to the present invention that the copper is at least partially present in metallic form (oxidation state = 0; Cu^0) and the promotor metal is at least partially present in oxidised form (oxidation state > 0 , preferably oxidation state = +1, like Na^+ and K^+ , and/or preferably oxidation state = +2, like Ca^{2+} and Sr^{2+}). Preferably $\geq 50 \text{ mol}\%$, more preferably $\geq 60 \text{ mol}\%$, still more preferably $\geq 70 \text{ mol}\%$ and even more preferably $\geq 80 \text{ mol}\%$ of the copper are present in metallic form, and/or preferably $\geq 60 \text{ mol}\%$, more preferably $\geq 70 \text{ mol}\%$, still more preferably $\geq 80 \text{ mol}\%$ and even more preferably $\geq 90 \text{ mol}\%$ of the promotor metal are present in oxidised form, respectively based on the total atomic composition of the catalyst. When the copper is at least partially present in metallic form and the promotor metal is at least partially present in oxidised form, especially in the above-indicated molar percentages, a good balance between the effects of the copper, in particular CO yield and a selective conversion of CO_2 to CO, and the effects of the promotor metal, in particular thermal stability, CO_2 activation, and suppression of methane formation, is achieved. The copper is especially present in the preferred metallic form when actually used in a CO_2 hydrogenation (or hydrogenation of CO_2). Beforehand, the copper may be present in oxidised form, especially as CuO. Such oxidised copper and especially CuO is typically reduced in-situ in a hydrogenation reaction, especially in a CO_2 hydrogenation by the hydrogen fed to the catalyst in such a reaction.

It is preferred for a catalyst according to the present invention that the catalyst is free of iron. For example, the catalyst according to the present invention comprises less than 0.1 wt.% iron, more preferably less than 0.01 wt.% iron, and still more preferably less than 0.001 wt.% iron, based on the total weight of the catalyst. Iron-based catalysts often promote Fischer-Tropsch syntheses. Depending on the feed for the CO_2 conversion using

the catalyst according to the present invention, such a Fischer-Tropsch synthesis may occur as an undesired simultaneous reaction which can disadvantageously reduce the CO yield and/or the selectivity towards CO. This can then also lead to problems during purification of the product of the CO₂ conversion. When the catalyst according to the present invention is free of iron, undesired simultaneous reactions like Fischer-Tropsch syntheses and problems associated therewith can be avoided.

It is also preferred for a catalyst according to the present invention that the catalyst is free of cerium and/or is free of zirconium. Cerium-doped and/or zirconium-doped catalysts may be comparably costly so that it is preferred that those elements are absent from the catalyst according to the present invention.

It is preferred for a catalyst according to the present invention that the catalyst has a (powder) X-ray diffraction ((P)XRD) pattern in which no reflections are observed which could be assigned to a promotor metal phase, wherein it is more preferred that no reflections are observed which could be assigned to a promotor metal oxide phase and still more preferred that no reflections are observed which could be assigned to a sodium oxide phase or a potassium oxide phase, respectively (when the XRD pattern is recorded after calcination of the catalyst with Co K_α radiation ($\lambda = 1.790 \text{ \AA}$) at 30 kV and 10 mA). When no such reflections are observed, the promotor metal is present in a preferred highly dispersed form, especially in the form of nano-crystallites and/or in an amorphous state. Without wishing to be bound to theory, it is assumed that with the promotor metal being present in a highly dispersed form, especially present in the form of nano-crystallites and/or in an amorphous state, the performance of the catalyst according to the present invention is further improved, especially in terms of thermal stability, CO₂ activation, and suppression of methane formation.

It is preferred for a catalyst according to the present invention that the catalyst has an activity of $\geq 30 \text{ } \mu\text{mol}_{\text{CO}_2} \text{ g}_{\text{Cu}}^{-1} \text{ s}^{-1}$ at 260 °C, more preferably of $\geq 33 \text{ } \mu\text{mol}_{\text{CO}_2} \text{ g}_{\text{Cu}}^{-1} \text{ s}^{-1}$ at 260 °C and still more preferably of $\geq 36 \text{ } \mu\text{mol}_{\text{CO}_2} \text{ g}_{\text{Cu}}^{-1} \text{ s}^{-1}$ at 260 °C. With such a continuously increasing activity, the productivity of the catalyst is continuously improved. The conditions under which such an activity is measured are in particular 20 bar(g), 1400 mL min⁻¹ g_{Cu}⁻¹, 2700-4000 h⁻¹ GHSV, 3.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%.

It is preferred for a catalyst according to the present invention that the catalyst has a CO selectivity at 240°C of $\geq 90\%$, more preferably of $\geq 95\%$ and still more preferably of $\geq 99\%$. It is more preferred for a catalyst according to the present invention that the catalyst has a CO selectivity at 200°C of $\geq 90\%$, more preferably of $\geq 95\%$ and still more preferably of $\geq 99\%$. With such an increased CO selectivity at low temperatures, the production of undesired by-products is advantageously lowered, and the product of a hydrogenation of CO₂ can be more easily purified, without requiring too high temperatures. The conditions under which such a CO selectivity is measured are in particular 40 bar(g), 700 mL min⁻¹ g_{Cu}⁻¹, 2000 h⁻¹ GHSV, 2.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%.

It is preferred for a catalyst according to the present invention that the catalyst has a turnover frequency (TOF) of $\geq 1.0 \times 10^{-2} \text{ s}^{-1}$ at a temperature of 260°C. With such an increased turnover frequency, the activity of the catalyst and hence its productivity is improved. As used in the art and herein, the turnover number (abbreviated TON) is the number of moles of substrate that a mole of catalyst can convert before becoming inactivated. The turnover frequency (abbreviated TOF) refers to the turnover per unit time. The relationship between turnover number and turnover frequency is thus $\text{TOF} = \text{TON}/t$.

Subject of the invention is also a method of producing carbon monoxide, comprising the steps:

- i) providing a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$,
- ii) feeding carbon dioxide and hydrogen to the catalyst, and
- iii) converting the carbon dioxide at least partially into carbon monoxide.

The preferred embodiments of the catalyst described herein including the claims are likewise preferred for the method according to the present invention in an analogous manner. Given that an rWGS reaction is carried out in step iii), this step will regularly also yield H₂O, i.e., it will regularly be a step of converting the carbon dioxide at least partially into carbon monoxide and water.

It is preferred for the method according to the present invention that step iii) is carried out at a temperature of $\leq 300^{\circ}\text{C}$, more preferably at a temperature of $\leq 260^{\circ}\text{C}$. Due to the use of the inventive catalyst, the CO_2 conversion and hence the CO yield remain high even at such comparably low temperatures. Also due to the use of the inventive catalyst, the selectivity towards CO is enhanced even at such comparably low temperatures. At the same time however, the energy efficiency of the entire method is improved because less heating is required in step iii) for the conversion of CO_2 into CO as this step can be carried out at consecutively lower temperatures of $\leq 300^{\circ}\text{C}$ and $\leq 260^{\circ}\text{C}$, respectively. Moreover, operating the method at the mentioned lower temperatures increases the lifetime of the catalyst so that less catalyst regeneration and/or catalyst replacement is required, which improves the economics of the method according to the present invention.

Subject of the invention is also a use of a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$, for catalysing a hydrogenation of CO_2 into CO. The preferred embodiments of the catalyst described herein including the claims are likewise preferred for the use according to the present invention in an analogous manner. Any use of a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$, described herein may also be considered as a corresponding method of using such a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$.

Brief description of the drawings

Fig. 1 shows a CO_2 conversion as a function of Time On Stream (TOS).
Fig. 2a shows a CO_2 conversion as a function of temperature.
Fig. 2b shows CO_2 conversion results at 200°C .
Fig. 2c shows CO_2 conversion results at 220°C .
Fig. 2d shows CO_2 conversion results at 240°C .

Fig. 2e shows CO₂ conversion results at 260°C.

Fig. 3a shows a CO selectivity as a function of temperature.

Fig. 3b shows CO selectivity results at 200°C.

Fig. 3c shows CO selectivity results at 220°C.

5 Fig. 3d shows CO selectivity results at 240°C.

Fig. 3e shows CO selectivity results at 260°C.

Fig. 4a shows X-ray diffractograms of fresh Cu-based catalysts supported on carbon and silica.

10 Fig. 4b shows X-ray diffractograms of Cu-based catalysts supported on carbon and silica after catalysis.

Fig. 5a shows a STEM-HAADF image, an EDX map and a particle size distribution.

Fig. 5b shows HAADF-STEM micrographs with corresponding elemental maps for carbon-supported and silica-supported catalysts.

Fig. 5c shows the HAADF-STEM images of Fig. 5b together with Cu and K EDX maps.

15 Fig. 5d shows single pixel counts in the K energy range of the EDX spectra of Fig. 5b.

Fig. 5e shows TEM images together with relative particle size distributions of copper-based catalysts.

Fig. 6 shows temperature-dependent H₂ reduction profiles.

Fig. 7a shows CO₂ conversion and CO selectivity of prepared catalysts.

20 Fig. 7b also shows CO₂ conversion and CO selectivity of prepared catalysts.

Fig. 7c shows an Arrhenius plot of CO₂ converted.

Fig. 8a shows CO₂ conversion and CO and MeOH selectivity for carbon-supported catalysts.

25 Fig. 8b also shows CO₂ conversion and CO and MeOH selectivity for carbon-supported catalysts.

Fig. 9a shows CO₂ conversion and CO selectivity for carbon-supported catalysts.

Fig. 9b also shows CO₂ conversion and CO selectivity for carbon-supported catalysts.

Fig. 10a shows CO selectivity for carbon-supported catalysts.

Fig. 10b also shows CO selectivity for carbon-supported catalysts.

30 Fig. 11a shows CO₂ conversion and weight-normalized copper time yield (CTY) for carbon-supported catalysts.

Fig. 11b also shows CO₂ conversion and weight-normalized copper time yield (CTY) for carbon-supported catalysts.

Fig. 12 shows transmission electron micrographs with corresponding particle size distributions.

Fig. 13 shows a comparison of CO selectivities of promoted copper catalysts.

Fig. 14 shows a comparison of activities of promoted copper catalysts.

5 Fig. 15 shows an overview of CO₂ conversion results.

Fig. 16a shows MeOH selectivity results at 200°C.

Fig. 16b shows MeOH selectivity results at 220°C.

Fig. 16c shows MeOH selectivity results at 240°C.

Fig. 16d shows MeOH selectivity results at 260°C.

10

Examples

Example 1

15 Catalyst synthesis

A carbon support is co-impregnated by a mixture of copper and potassium or sodium precursors. More specifically, an aqueous solution containing Cu and K or Na nitrates is contacted with a dry carbon support. The solution volume amounts to 95 % of the support
20 pore volume and is adsorbed by the support upon mixing. The as-prepared material subsequently undergoes a series of drying and reduction steps before being used as a catalyst for rWGS.

More specifically, copper-promotor metal catalysts according to the present invention are
25 prepared using the incipient wetness co-impregnation technique. A detailed recipe for the preparation of CuK/GNP containing 9 wt% Cu and 0.6 wt% K is as follows: For a typical impregnation, 1.5 g GNP500 were dried at 170 °C under dynamic vacuum for 2 hours. Herein, GNP is short for GNP500, an ordered graphitic material of roughly 500 m² g⁻¹ surface area which has been applied as carbonaceous support. The vacuum was partially
30 released and impregnated directly afterwards with a 95% pore-filling amount of precursor solution consisting of 0.568 g Cu(NO₃)₂•3H₂O and 0.0238 g KNO₃ in 0.1M HNO₃. The solution was added dropwise under magnetic stirring. After the addition, the powder was dried at room temperature for 24 hours under dynamic vacuum.

In the prepared catalysts, the Cu weight loading amounted to 9 wt.%, while the Cu:promotor metal atomic ratio was set at 10:1, as shown in Table 1 below. The reported weight loadings were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Table 1 further indicates that particle sizes of the fresh catalysts lie within the same range as determined from XRD measurements.

Table 1 – Targeted metal weight loadings and measured particle size of Cu/GNP, CuK/GNP and CuNa/GNP (with X = Na or K, respectively)

Name	Cu (wt%)	X (wt%)	Fresh Particle size $d_s \pm \sigma_{ds}$ (nm)
Cu/C	9.0	---	7.1 ± 2.5
Cu-Na ₂ O/C	9.0	0.3	7.4 ± 2.1
Cu-K ₂ O/C	9.0	0.6	8.5 ± 2.5

To avoid exposure to air, the dried impregnated powder was stored in an argon(Ar)-filled glovebox. The dried sample, loaded in a plug-flow reactor, was dried under flowing nitrogen (150 ml min^{-1}) for 1 h at 280°C (1°C min^{-1}). Next, the catalyst was slowly passivated under flowing 10 vol% O₂/N₂ mixture (150 ml min^{-1}) for 3 h at room temperature.

The catalysts were pressed and sieved to a grain size of 75-150 μm . More specifically, the powdered catalysts were pelletized under a pressure of 2 tons and were then crushed and sieved. The sieved fraction of 75-150 μm was the powder remaining in between the 75 μm and 150 μm sieves.

Catalyst testing

As shown in the accompanying Figs., the catalyst achieves a remarkable performance at temperatures as low as 260°C . Fig. 1 shows a CO₂ conversion as a function of Time On Stream (TOS) at $180\text{-}260^\circ\text{C}$, 40 bar and H₂:CO₂ = 3 using Cu/GNP, CuZrO₂/GNP and CuK₂O/GNP catalysts. Namely, Fig. 1 shows the CO₂ conversion obtained on CuK/GNP at temperatures between 180 and 260°C in addition to those of a reference Cu/GNP catalyst and CuZr/GNP catalyst of similar metal weight loading. Fig. 1 highlights the

positive impact of copper promotion by potassium in addition to comparative elements such as zirconium, while no significant catalyst deactivation was observed.

However, not all elements lead to an improvement in activity as shown in Fig. 2a, depicting the CO₂ conversion as a function of temperature. The actually applied conditions were: H₂/CO₂/He = 67.5/22.5/10 vol%, 3.2 mg Cu per reactor, Cu:Promoter=1:10. More specifically, Fig. 2a shows a CO₂ conversion as a function of temperature at 40 bar and H₂:CO₂ = 3 using unpromoted Cu/GNP and various promoted CuX/GNP catalysts, with X representing the elements in the legend. Besides K (and partly Zr), Na also significantly promotes the catalytic activity. Figs. 2b to 2e provide individual illustrations of the data points of Fig. 2a separately for the temperatures 200°C, 220°C, 240°C and 260°C, respectively.

The impact on product selectivity is also element-specific as shown in Fig. 3a. The actually applied conditions were: H₂/CO₂/He = 67.5/22.5/10 vol%, 3.2 mg Cu per reactor, Cu:Promoter=1:10. Fig. 3a actually shows CO selectivity as a function of temperature at 40 bar and H₂:CO₂ = 3 using unpromoted Cu/GNP and various promoted CuX/GNP catalysts, with X representing the elements in the legend. By using Na and K as promoter metals, the catalyst is able to reach 97+ % selectivity to CO. At 240 °C, a CO₂ conversion of 15 % matches the thermodynamic limit of rWGS at 40 bar and H₂:CO₂ = 3. The remaining product was detected as methanol, while formation of the undesirable by-product methane was not observed. It is further seen from Fig. 3a that Ca, Mg and Sr can also improve the CO₂ selectivity, especially at a temperature of 260 °C or less. Figs. 3b to 3e provide individual illustrations of the data points of Fig. 3a separately for the temperatures 200°C, 220°C, 240°C and 260°C, respectively.

In Fig. 13, a comparison of the CO selectivities at 260°C, 40 bar, of the alkali-promoted catalysts with those of the alkaline-earth-promoted catalysts and a pure copper catalyst, respectively, is provided. It is seen from the presented results that addition of alkali or alkaline earth promoters increases the CO selectivity in comparison to the unpromoted Cu/C catalyst.

In, Fig. 14 a comparison of the activities, in terms of weight-normalized copper time yield (CTY), at 260°C, 40 bar, of the alkali-promoted catalysts with those of the alkaline-earth-promoted catalysts and a pure copper catalyst, respectively, is provided. It is seen from the presented results that addition of K₂O, Na₂O and SrO increases the activity in comparison to the unpromoted Cu/C catalyst.

Fig. 15 provides an overview of the CO₂ conversion results at 240°C (H₂/CO₂/He = 67.5/22.5/10; 2.2 mL/min per reactor, 40 bar(g); Cu:Promoter=1:10) for the tested catalysts and their selectivities for carbon monoxide and methanol (MeOH), respectively. It is seen from the presented results that addition of alkali or alkaline earth promoters increases the selectivity for CO and decreases the selectivity for MeOH in comparison to a pure copper catalyst as well as in comparison to a Ce-doped catalyst and a Zr-doped catalyst.

Figs. 16a to 16d provide individual illustrations of the MeOH selectivities of the tested alkali and alkaline earth-promoted catalysts separately for the temperatures 200°C, 220°C, 240°C and 260°C, respectively.

Example 2

Catalyst synthesis

Supported potassium or sodium promoted copper-based catalysts were prepared via incipient wetness (co-)impregnation of either a graphitic carbon (XG Sciences, GNP500, 440 m² g⁻¹) or a silica gel (25-75 µm, Davisil™, grade 643, Sigma Aldrich, ≥99%) support. 1.5 g of support was dried under dynamic vacuum for 2 h at 170 °C, for the carbon support or at 230 °C, for the silica support. 95% of the support's total pore volume was impregnated with ca. 1.38-2.58 M copper nitrate (Acros Organics, ≥99%) and ca. 0.15-0.26 M potassium nitrate (Sigma Aldrich, ≥99%) or 0.26 M sodium nitrate (Thermo Scientific, ≥99%) in a 0.10 M HNO₃ aqueous solution aiming to a 1:10 promoter:copper atomic ratio. After drying under dynamic vacuum for 24 h, the nitrate precursor species were decomposed at 280 °C (2 °C min⁻¹) in N₂ flow of 200 mL min⁻¹ g⁻¹ for 1.5 h, while the silica-supported samples were heat-treated at 300 °C (2 °C min⁻¹) in 1% NO/N₂ flow of 600 mL min⁻¹ g⁻¹ for 1 h. The heat treatment temperature and 1% NO/N₂ gaseous

atmosphere were set to achieve a relatively narrow particle size distribution. Furthermore, to ensure full oxidation of the Cu nanoparticles supported on carbon and allow XRD analysis, the carbon-supported catalysts were calcined at 240 °C (1 °C min⁻¹) for 1 h under a flow of 200 mL min⁻¹ 10 vol% O₂/N₂. The catalysts were named CuX/Y, in which X identifies the promoter present and Y the type of support; carbon (C) or silica (SiO₂).

Catalyst characterisation

Transmission electron microscopy (TEM) was performed on a Thermo Fisher Scientific Talos L120C instrument, operated at 120 kV. The TEM samples were prepared by dry loading, putting in contact with the wholly carbon-coated Cu grids (Agar, 300 mesh) the pre-ground sample. The surface averaged Cu particle size (d_s) was calculated based on the measurement of at least 200 individual particles at various locations within the sample.

High-angle annular dark-field scanning TEM (HAADF-STEM) measurements were performed on a Thermo Fisher Scientific Talos F200X apparatus (operated at 200 kV) equipped with a Super-X G2 energy-dispersive X-ray (EDX) detector. The HAADF-STEM-EDX samples were prepared by suspending the sample in absolute ethanol using sonication. The suspension was drop-casted on a wholly carbon-coated Au grids (Agar, 300 mesh).

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D2 Phaser instrument (Co K α radiation (λ = 1.790 Å) at 30 kV and 10 mA). The used catalysts were exposed to ambient conditions and separated from the SiC before the measurement. The CuO crystallite sizes were calculated with the 42° XRD peak considering the instrumental line broadening.

Temperature-programmed reduction (H₂-TPR) experiments were performed on a Micromeritics AutoChem II 2920 instrument, equipped with a thermal conductivity detector (TCD). After 30 minutes of drying at 120 °C under 50 mL min⁻¹ flow of Ar, the catalysts (approximately 40 mg) were cooled down to room temperature. The dried catalysts were then exposed to a 25 mL min⁻¹ flow of 5 vol% H₂/Ar while heating to 700 °C (2.5 °C min⁻¹ ramp rate).

Catalyst testing

Catalytic experiments were performed in an Avantium Flowrence 16 parallel fixed-bed reactor setup. Stainless-steel reactors (2.6 mm ID) were loaded either with ca. 2.2 or
5 3.2 mg of copper (75-150 μm sieve fraction) mixed with inert SiC (212-425 μm sieve fraction), resulting in a SiC content of approximately 80 vol% of the total packed bed. Two separate catalytic tests were performed to evaluate the performance of the catalysts for CO_2 hydrogenation reaction. In both tests, before catalysis, the catalysts were reduced at atmospheric pressure at 250 $^\circ\text{C}$ (2 hours, 2.5 $^\circ\text{C min}^{-1}$) in a 10.9 mL min^{-1} flow of 10 vol%
10 H_2/N_2 .

In the first test, the performance of the catalysts was evaluated at 20 bar and temperature between 180 and 260 $^\circ\text{C}$ in three different feeds $\text{H}_2:\text{CO}_2:\text{He}$, with the feed progressively containing lower $\text{H}_2:\text{CO}_2$ ratios starting from 9:1 to 3:1 and finally to 1:1 ratio. In detail,
15 after *in-situ* reduction, the catalysts were exposed to a 3.1 mL min^{-1} flow of $\text{H}_2/\text{CO}_2/\text{He} = 81/9/10$ vol%. The reactors were pressurized to 20 bar and heated to 240 $^\circ\text{C}$ (5 $^\circ\text{C min}^{-1}$ ramp rate). The temperature was changed stepwise every 7.5 hours from 180 to 260 $^\circ\text{C}$ in steps of 20 $^\circ\text{C}$. After 46 hours, the catalysts were exposed to a 3.1 mL min^{-1} flow of $\text{H}_2/\text{CO}_2/\text{He} = 67.5/22.5/10$ vol% ($\text{H}_2:\text{CO}_2=3:1$), and the temperature was varied again
20 between 200 and 260 $^\circ\text{C}$. Finally, after 86 hours, the atmosphere was switched to $\text{H}_2/\text{CO}_2/\text{He} = 45/45/10$ vol% ($\text{H}_2:\text{CO}_2=1:1$) and a similar temperature protocol was applied with temperatures varying between 220 and 280 $^\circ\text{C}$.

In the second catalytic test the catalysts' performance, namely conversion and selectivity,
25 in $\text{H}_2/\text{CO}_2/\text{He} = 67.5/22.5/10$ vol% feed (3:1= $\text{H}_2:\text{CO}_2$ ratio) were further explored at 40 bar and at temperatures between 180 and 260 $^\circ\text{C}$. After *in-situ* reduction, the catalysts were exposed to a 2.2 mL min^{-1} flow of $\text{H}_2/\text{CO}_2/\text{He} = 67.5/22.5/10$ vol%. The reactors were pressurized to 40 bar and heated to 240 $^\circ\text{C}$ (5 $^\circ\text{C min}^{-1}$ ramp rate). After 25 hours the temperature was lowered to 180 $^\circ\text{C}$ and consecutively increased in steps 20 $^\circ\text{C}$ to 260 $^\circ\text{C}$.
30 Reaction products were analyzed every 14 min, by online gas chromatography (Aligent 7890B) equipped with one thermal conductivity detector and two flame ionization detectors.

Structural properties and reduction of the catalyst

The structural properties of the (promoted) copper-based catalysts before catalysis were investigated by XRD, TEM and STEM-HAADF-EDX and are summarized in Table 2.

5

Table 2 - Structural properties of the copper-based catalysts

Catalyst	Atomic Ratio	Loading		Particle diameter		Cu dispersion (%) [a]
	Promoter:Cu	Cu (wt. %)	Promoter (wt. %)	XRD d_v (nm)	TEM $d_s \pm \sigma_{ds}$ (nm)	
Cu/C	-	9	-	11.9	7.6 ± 2.7	13.7
CuK/C	1:10	9	0.6	14.0	8.9 ± 2.7	11.7
CuNa/C	1:10	9	0.3	6.8	8.1 ± 2.4	12.8
Cu/SiO ₂	-	8.5	-	11.7	15.1 ± 4.9	6.9
CuK/SiO ₂	1:10	9	0.6	10.6	12.4 ± 3.6	8.4

[a] Cu dispersion (%) was calculated using the surface averaged particle size (d_s) of the fresh catalysts determined by TEM analysis.

10

Note that the ratio between copper surface atoms and total copper atoms (Cu dispersion %) was calculated according to the following equation:

$$Cu \text{ dispersion } (\%) = \frac{6V_m}{A_m * d_s}$$

where V_m is the molar volume of the copper particles $7.09 \times 10^{21} \text{ nm}^3$, A_m is the molar area of the copper particles $4.10 \times 10^{22} \text{ nm}^2$ and d_s is the surface averaged particle size (nm) of the fresh catalysts.

15

In Fig. 4a, X-ray diffractograms of the fresh copper-based catalysts supported on (a) carbon and on (b) silica are presented. The diffractograms are vertically stacked for visual clarity. The XRD patterns show only peaks that can be assigned to the CuO phase and the support, either silica or carbon. None of the promoted catalysts showed reflections of potassium oxide or sodium oxide phases. The absence of reflections in XRD indicates that K and Na exist in a highly dispersed form as nano-crystallites or in an amorphous

20

state. The same conclusion can be drawn from the X-ray diffractograms of the fresh copper-based catalysts after catalysis shown in Fig. 4b, again supported on (a) carbon and on (b) silica, respectively. None of the promoted catalysts showed reflections of potassium oxide or sodium oxide phases, indicating that K and Na species are present in a highly dispersed or amorphous state.

In Fig. 5a, an STEM-HAADF image, a corresponding EDX map and particle size distribution of the (a,b,c) fresh CuK/C and the (d,e,f) fresh CuK/SiO₂ catalysts are presented. The HAADF-STEM-EDX analysis confirmed the presence of highly dispersed K over the carbon support (Fig. 5a, frame b) and the silica support (Fig. 5a, frame e) in coexistence with CuO nanoparticles. Elemental mapping of the CuNa/C catalysts was impossible due to the overlapping between the characteristic L α peak of Cu at 0.930 KeV and the K β peak belonging to Na at 1.041 KeV. TEM analysis, of the carbon-supported catalysts, showed highly dispersed nanoparticles on the graphitic carbon sheets in the range of 7-9 nm regardless of the promoter presence. While, on a silica support, several large agglomerations of CuO were found in coexistence with nanoparticles with an average particle size of 15 nm for the unpromoted catalysts and 12 nm for the K-promoted catalyst. The larger average particle size and the presence of large Cu agglomeration on silica are likely to be related to the lower support surface area (268 m² g⁻¹ for SiO₂ VS 440 m² g⁻¹ for carbon) and the higher temperature adopted during the catalyst's synthesis (300 °C for SiO₂ VS 280 °C for carbon supported catalysts).

Fig. 5b shows representative HAADF-STEM micrographs with the corresponding elemental maps for the carbon-supported (frame a-h) and the silica-supported (frame i-p) catalysts. More specifically, Fig. 5b shows HAADF-STEM images, corresponding EDX maps and EDX spectra of the (a-d) fresh and (e-h) used CuK/C and the (i-l) fresh and (m-p) used CuK/SiO₂ catalysts. EDX spectra were extracted from two different areas of the sample. Area 1 (upper line) at the Cu nanoparticles location, Area 2 (lower line) at the support without Cu nanoparticles, and at the background (dashed line) is taken in an area of the grid where no catalyst was present. Each elemental maps were acquired for a total time of approximately 30 minutes, except for the used CuK/SiO₂ catalyst that was acquired for 9'21" total time.

For the map of individual elements see Fig. 5c. More specifically, Fig. 5c shows the HAADF-STEM images of Fig. 5b together with Cu and K EDX maps of the (a-c) fresh and (d-f) used CuK/C and the (g-i) fresh and (j-l) used CuK/SiO₂ catalysts. As potassium is a light element, the signal to noise ratio in the EDX map is low, see Fig. 5d. More specifically, Fig. 5d presents single pixel counts in the potassium energy range after averaging over 4x4pixels area (hence 16 pixels). The EDX spectra correspond to the elemental maps in Fig. 5b and show the CuK/C catalyst in the (a) fresh and (b) used state and the CuK/SiO₂ catalyst in the (c) fresh and (d) used state. To analyse the EDX data in more detail, for each elemental map the EDX spectra at sample locations with and without Cu and/or support were directly compared. Area 1 corresponds to the Cu nanoparticles' location whereas Area 2 corresponds to an area of the support without Cu nanoparticles, while also the spectrum taken in an area of the grid without catalyst is shown (black line). In the carbon-supported catalyst, either in the fresh (Fig. 5b, frame c) or used state (Fig. 5b, frame g), only at the Cu nanoparticles' location (Fig. 5b, Area 1) a significant K-signal was observed while on the bare support (Fig. 5b, Area 2) no significant K is detected. On the contrary in the silica-supported catalyst (Fig. 5b, frame k) a significant amount of K was detected both on locations of the copper nanoparticles as well as on the bare support. The EDX spectra of the used catalysts (Fig. 5b, frame o) shows no significant changes in the promoter distribution upon catalysis. Therefore, the relatively high potassium signal over the silica support (Fig. 5b, Area 2 in frames k and o) are ascribed to the presence of alkali metal silicates, which remained stable under reaction conditions. These measurements clearly show that the carbonaceous support enforces a close intimacy between the metal nanoparticles and the promoter when compared to an oxidic support such as SiO₂. Elemental mapping of the CuNa/C catalysts was not possible due to the overlap between the characteristic K_β peak belonging to Na at 1.041 KeV and the L_α peak of Cu at 0.929 KeV.

Fig. 5e shows representative (a, c, e, g, i) TEM images with (b, d, f, h, j) relative particle size distribution of unpromoted and promoted copper-based catalysts in the fresh state. The TEM analysis of the carbon-supported catalysts showed well-distributed nanoparticles in the size range of 7-9 nm on the graphitic carbon sheets regardless of the promoter presence. On the silica support, larger agglomerates of CuO were found in coexistence with nanoparticles with an average particle size of 15 nm for the unpromoted catalysts and 12 nm for the K-promoted catalyst. Furthermore, the CuK/SiO₂ catalyst

showed a narrower particle size distribution than the unpromoted Cu/SiO₂ catalyst. The larger average particle size and the presence of large Cu agglomeration on silica are probably due to the higher density of Cu atoms on silica (3 Cu atoms per nm² for SiO₂ versus 2 Cu atoms per nm² for carbon) and the higher temperature applied during the catalyst synthesis (300 °C for SiO₂ versus 280 °C for carbon supported catalysts).

In Fig. 6, temperature-dependent H₂ reduction profiles are presented which are vertically stacked for visual clarity. More specifically, the reducibility of copper was studied by H₂-TPR experiment, and the profiles are reported in Fig. 6. The unpromoted catalysts show a peak at 180 °C and 167 °C for the silica and carbon support, respectively. The higher temperature required for CuO reduction on oxidic support is correlated to the larger fraction of bulk-like CuO phases. Upon addition of an alkali promoter the reduction peak of CuO shifts to higher temperatures, i.e., from 167 °C for Cu/C to 190 °C for CuK/C. In particular, the higher temperature required for CuO reduction on silica may be ascribed to various phenomena: the presence of some macrocrystalline CuO which is more difficult to reduce, the higher hydrophilicity of SiO₂ which induces a stronger retention of *in situ* generated water and/or a stronger interaction of CuO with the oxidic support than with carbon. For all the catalysts, the addition of an alkali promoter significantly lowers the CuO reduction rate shifting the peak to higher temperatures. Upon addition of K, the peak temperature shifted 33 °C for the carbon-supported catalysts and to 48 °C for the silica-supported catalysts. Without wishing to be bound to theory, the effect of alkali promoter on Cu reducibility, in particular K, can be related to an electronic effect induced by K/KO_x in proximity to the CuO nanoparticles, i.e. electron donation from K to Cu. The H₂-TPR measurements are of importance as they show that the majority of the Cu-based nanoparticles are in contact with promoter species, as otherwise the reduction temperature of CuO would not be influenced significantly. Also, the slower reduction kinetics might indicate a lower hydrogenation activity of the Cu catalyst.

Catalytic performances of catalysts

First analysis of catalytic performances

5 In Fig. 7a, (a) CO₂ conversion (%) and (b) CO selectivity (%) for the prepared catalysts are presented as a function of temperature. The applied conditions were 20 bar(g), 1400 mL min⁻¹ g_{Cu}⁻¹, 2700-4000 h⁻¹ GHSV, 3.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%. The thermodynamic equilibrium lines in Fig. 7a only take CO and H₂O as products into account, i.e., only the products of the rWGS reaction (without by-products). Fig. 7a, frame
10 a, shows the CO₂ conversion at 20 bar(g) under different temperature (200-260 °C). The unpromoted catalysts show similar CO₂ conversion, with conversion increasing with increasing temperature. At high temperatures, the Cu/SiO₂ shows slightly higher activity in comparison to the Cu/C catalyst. At 260 °C, the Cu/SiO₂ activity was 23.1 μmol_{CO2} g_{Cu}⁻¹ s⁻¹ while for the Cu/C the activity was 16.7 μmol_{CO2} g_{Cu}⁻¹ s⁻¹. The addition of a small amount
15 of K (0.6 wt. %) to the silica-supported catalyst leads to a slight decrease in the catalyst's activity in comparison to the unpromoted Cu/SiO₂ catalysts at a temperature between 240 and 260 °C. On the contrary, the CO₂ conversion of the carbon-supported catalysts increases after the addition of K at all the temperatures tested. Remarkably, the activity doubled upon the addition of K. The CuK/C shows an activity of 38.1 μmol_{CO2} g_{Cu}⁻¹ s⁻¹ at
20 260 °C. The activity enhancement by promoter incorporation on carbon-supported copper catalysts was also achieved by the addition of 0.3 wt. % of Na. The CuNa/C catalysts show enhanced CO₂ conversion in comparison to the unpromoted Cu/C along all the temperatures tested, reaching the highest activity of 36.5 μmol_{CO2} g_{Cu}⁻¹ s⁻¹ at 260 °C. The opposite effect on activity after promoter incorporation between the silica and carbon-
25 supported catalysts is likely to be related to the different support surface area (268 m² g⁻¹ for SiO₂ VS 440 m² g⁻¹ for carbon). Likely because of its higher surface area carbon could accommodate more promoters, preventing coverage of the copper active sites.

Besides activity, the addition of a promoter to the catalyst's formulation could also
30 influence product distribution. At 20 bar(g) and 200-260 °C, MeOH and CO are the two main products in an H₂:CO₂=3 feed over selective copper-based catalysts. Thermodynamic calculation (without considering CH₄ formation) reveals that, at 20 bar(g) and 200 °C, MeOH is the main product with a selectivity of 77% and the rest being CO. At higher temperatures, CO becomes the predominant product reaching a selectivity of 82 %

at 260 °C. Fig. 7a, frame b, reports the CO selectivity (%) as a function of temperature for the synthesized catalysts.

All the catalysts show very high CO selectivity. More importantly, the Sabatier reaction (reaction of H₂ with CO₂ to yield CH₄) was completely suppressed. Only traces of CH₄ were detected (lower than 0.2 % CH₄ selectivity). CO selectivity was above 90 % for all the catalysts with MeOH being the main by-product. Both promoters tested (K and Na) show an enhancement of the selectivity to CO in comparison to the unpromoted catalysts regardless of the support used. Remarkably, K completely suppress MeOH formation leading to ~100 % CO selectivity at all the temperatures tested.

Second analysis of catalytic performances

Fig. 7b shows (a) CO₂ conversion (%) and (b) CO selectivity (%) for unpromoted and K and Na promoted Cu catalysts on either silica or carbon supports as a function of temperature (200-260 °C), under conditions of 20 bar(g), 1400 mL min⁻¹ g_{Cu}⁻¹, GHSV 2700-4000 h⁻¹, 3.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%. Thermodynamic CO₂ conversion (%) and CO selectivity (%) were calculated with HSC9 software considering a H₂/CO₂/He = 67.5/22.5/10 vol% feed and CO, CH₃OH and CO₂ as carbonaceous species. All catalysts show a close to exponentially increasing conversion with increasing temperature, except for CuK/C which reaches close to equilibrium conversion. For the silica-supported catalyst, the addition of K (9 at. % to Cu corresponds to a Cu surface coverage of 0.13 assuming that all K would be evenly spread over the Cu surface) led to a slight decrease in activity at temperatures between 240 and 260 °C. The apparent activation energies that are derived from this temperature-dependent activity are 103 ± 2 kJ/mol and 79 ± 2 kJ/mol for the Cu/SiO₂ and CuK/SiO₂. In this respect, see also Fig. 7c which shows an Arrhenius plot of CO₂ converted expressed as weight-normalized rate for unpromoted and K and Na promoted Cu catalysts on either silica or carbon supports. The average of the two data points at same conditions were used. The applied conditions were: 20 bar(g), 200-260 °C, 1400 mL min⁻¹ g_{Cu}⁻¹, GHSV 2700-4000 h⁻¹, 3.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%. The following Table 3 summarizes the apparent activation energies of the catalysts of Fig. 7c.

Table 3 – Apparent activation energies of tested catalysts

Catalyst	Apparent activation energy (kJ/mol)
Cu/C	63 ± 14
CuK/C	61 ± 9
CuNa/C	80 ± 5
Cu/SiO ₂	103 ± 2
CuK/SiO ₂	79 ± 6

For the carbon-supported catalysts, the CO₂ conversion greatly increased with the addition of K or Na at all temperatures. Assuming that all K or Na would be evenly spread
 5 over the Cu surface, the ratio of promoter/Cu_{surface} atoms corresponds to 0.09 and 0.04 for the CuK/C and CuNa/C catalysts, respectively. The CuK/C showed an activity of 38.1 $\mu\text{mol}_{\text{CO}_2} \text{g}_{\text{Cu}}^{-1} \text{s}^{-1}$ at 260 °C, while for Cu/C the activity was only 16.7 $\mu\text{mol}_{\text{CO}_2} \text{g}_{\text{Cu}}^{-1} \text{s}^{-1}$. The addition of 0.3 wt. % Na led to an activity of 36.5 $\mu\text{mol}_{\text{CO}_2} \text{g}_{\text{Cu}}^{-1} \text{s}^{-1}$ at 260 °C. The apparent activation energies are 63 ± 14 kJ/mol and 61 ± 9 kJ/mol for the Cu/C and
 10 CuK/C, respectively. These results strongly suggest that the promotion lowers the activation energy.

Without wishing to be bound to theory, the fact that for the silica-supported catalyst the alkali promotion is much less effective is probably explained by the lower metal-promoter
 15 intimacy obtained in comparison to the carbon-supported catalysts. A significant amount of the potassium is immobilised on the oxidic support, likely in the form of alkali metal silicates, distant from the Cu nanoparticles, as observed in the EDX spectra of the used catalysts (Fig. 5b, frame o), hampering the formation of highly active sites at the metal-promoter interfaces.

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The addition of a promoter can also influence the product distribution. At 20 bar(g) and 200-260 °C, MeOH and CO are the two main products in an H₂:CO₂=3 feed over selective copper-based catalysts. Calculation of the equilibrium gas composition (without considering CH₄ formation) shows that at 20 bar(g) and 200 °C, MeOH would be the main

product with a selectivity of 77% with the rest being CO. At higher temperatures, CO becomes the predominant product reaching an equilibrium product selectivity of 82 % at 260 °C. Fig. 7b, frame b, reports the experimental and calculated equilibrium CO selectivities (%) as a function of temperature. Surprisingly, all catalysts experimentally show much higher CO selectivities than the calculated equilibrium composition: the CO selectivity was above 90 % for all catalysts, with MeOH being the main by-product. Only traces of CH₄ were detected (lower than 0.2 % CH₄ selectivity). Both alkali promoters tested (K and Na) gave a large enhancement of the selectivity to CO in comparison to the unpromoted catalysts regardless of the support used. Remarkably, K almost completely suppressed MeOH formation leading to ~100 % CO selectivity at all temperatures tested. Remarkably, the Cu-based catalysts promoted by alkali supported on carbon presented in this work showed superior performance, combining a very high selectivity to CO with a large improvement in activity.

Carbon-supported catalysts' performances in different gas feeds (H₂:CO₂=9,3,1)

First analysis of performances in different gas feeds

In Fig. 8a, (a) CO₂ conversion (%) and (b) CO and MeOH selectivity (%) for the carbon-supported catalysts in feeds with different H₂:CO₂ ratio are presented. Here, 9:1 is H₂/CO₂/He = 81/9/10 vol%, 3:1 is H₂/CO₂/He = 67.5/22.5/10 vol%, and 1:1 is H₂/CO₂/He = 45/45/10 vol%. Conversion and selectivity values are reported in %, and the applied conditions were 20 bar(g), 260 °C, 1400 mL min⁻¹ g_{Cu}⁻¹, 4000 h⁻¹ GHSV, 3.2 mg Cu. The thermodynamic equilibrium lines in Fig. 8a only take CO and H₂O as products into account, i.e., only the products of the rWGS reaction (without by-products). Given the elevated activity and CO selectivity of the promoted carbon-supported copper-based catalysts for the rWGS, it was decided to investigate the effect of feed composition (H₂:CO₂ ratio) on catalysts' performance. Using excess H₂ can be a viable way of achieving higher conversions and matching downstream application CO/H₂ mixture requirements without additional separation needed.

The catalysts performance of carbon-supported catalysts was assessed at 20 bar(g) and 260 °C for H₂:CO₂ ratios ranging from 1:1 to 9:1. The positive influence of increasing H₂:CO₂ ratio on conversion can be seen in Fig. 8a, frame a. All the synthesized carbon-

supported catalysts show an increase in the CO₂ conversion with an increasing amount of hydrogen in the feed. A higher concentration of hydrogen in the feed enhances the rWGS reaction because excess of reducing agent (H₂) facilitates the reduction of CO₂ to CO. In all the different feeds the CO₂ conversion doubled upon the addition of K or Na. Furthermore, the presence of K completely suppressed the MeOH and CH₄ side reactions in all feed compositions. These remarkable results illustrate the great potential of K and Na promoted Cu/C catalyst for the low-temperature rWGS reaction in a broad range of feed compositions (H₂:CO₂ ratio).

Second analysis of performances in different gas feeds

Given the excellent activity and CO selectivity of the alkali-promoted carbon-supported copper-based catalysts for the rWGS, the effect of the H₂:CO₂ ratio (varying from 1:1 to 9:1) on the catalysts performance was investigated. Using an excess of H₂ is a strategy to achieve higher conversions and match H₂:CO ratio requirements of downstream applications (subsequent conversions). Fig. 8b shows (a) CO₂ conversion (%) and (b) CO, CH₄ and MeOH selectivity (%) for the carbon-supported catalysts in feeds with different H₂:CO₂ ratio: 1:1 is H₂/CO₂/He = 45/45/10 vol%, 3:1 is H₂/CO₂/He = 67.5/22.5/10 vol%, and 9:1 is H₂/CO₂/He = 81/9/10 vol%. Conversion and selectivity values are reported in %. The applied conditions were: 20 bar(g), 260 °C, 1400 mL min⁻¹ g_{Cu}⁻¹, GHSV 4000 h⁻¹, 3.2 mg Cu. Thermodynamic CO₂ conversion (%) were calculated with HSC9 software considering the experimental feeds and CO, CH₃OH and CO₂ (upper dashed lines) or CO and CO₂ (lower dashed lines) as carbonaceous species. The performance of carbon-supported catalysts was assessed at 20 bar(g) and 260 °C, see Fig. 8b. In frame a of Fig. 8b, all carbon-supported catalysts show that in all feeds the CO₂ conversion at least doubled upon the addition of K or Na. For the promoted catalysts it is close to, and limited by, the equilibrium conversion (no CH₄ formation taken into account).

Also, an increase in CO₂ conversion with an increasing amount of hydrogen in the feed is observed. From a thermodynamic point of view, increasing the H₂:CO₂ ratio from 1 to 3 to 9 leads to a higher CO₂ equilibrium conversion because the methanol synthesis becomes more favored (indicated in Fig. 8b, frame a). However, the promoted catalysts according to the present invention steered the product formation to CO rather than CH₄ or MeOH even at 9:1 H₂:CO ratios (frame b). Hence this does not explain the increase in conversion

with increasing H₂ content. It rather points to the fact that the reaction order in H₂ is positive. In other words, the dissociative adsorption of H₂ is a limiting step in this conversion. In the presence of K, no significant MeOH or CH₄ formation was observed suggesting that these pathways are kinetically hindered. Moreover, the catalyst operates at the thermodynamic limit for rWGS. These remarkable results illustrate the great potential of promoted Cu/C catalysts, especially of K-promoted and Na-promoted Cu/C catalysts, for the low-temperature rWGS reaction in a broad range of feed compositions (H₂:CO₂ ratio).

Carbon-supported catalysts' performances at higher pressure (40 bar(g))

First analysis of performances at higher pressures

The performances of the promoted carbon-supported copper-based catalysts were further investigated at higher pressure (40 bar(g)) in a similar temperature range (200-260 °C) as reported above for the catalytic performances of catalysts. In such conditions, from a thermodynamic point of view, MeOH formation is favoured in comparison to CO formation with a MeOH selectivity above 45% in the entire temperature range. Important to notice, in the catalytic test at 40 bar(g) the GHSV was halved in comparison to the test at 20 bar(g), from 4000 h⁻¹ to 2000 h⁻¹. Low GHSV will give a long contact time of reactant gas with catalytic active sites favouring MeOH formation over CO. Therefore, testing the catalysts in these MeOH synthesis favouring conditions represents a good way to evaluate the potential of alkali (K and Na) as promoters for high-pressure rWGS reaction.

In Fig. 9a, (a) CO₂ conversion (%) and (b) CO selectivity (%) for the carbon-supported catalysts are presented as a function of temperature. The applied conditions were 40 bar(g), 700 mL min⁻¹ g_{Cu}⁻¹, 2000 h⁻¹ GHSV, 2.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%. The thermodynamic equilibrium lines in Fig. 9 only take CO and H₂O as products into account, i.e., only the products of the rWGS reaction (without by-products). Fig. 9, frame a, shows the CO₂ conversion at 40 bar(g) under different temperatures (200-260 °C). All the tested catalysts show an increase in CO₂ conversion with increasing temperature. At 220 °C, the activity of the catalysts was in the order 11.9 μmol_{CO2} g_{Cu}⁻¹ s⁻¹ for CuK/C > 8.2 μmol_{CO2} g_{Cu}⁻¹ s⁻¹ for CuNa/C > 4.5 μmol_{CO2} g_{Cu}⁻¹ s⁻¹ for Cu/C. The activity increases 2/3-fold upon the addition of Na or K, respectively.

At 40 bar(g), the difference in product distribution was very marked between the promoted and un-promoted catalysts at all the temperatures tested as reported in Fig. 9a, frame b. CO and MeOH were the only two products detected in relevant quantities. Only traces of CH₄, up to 0.7 % selectivity, were detected for the Cu/C and CuNa/C catalysts. On the one hand, the CO selectivity for the unpromoted Cu/C catalysts increases from 47 to 82 % with increasing temperature, as expected from thermodynamics due to the endothermic nature of the rWGS reaction. On the other hand, the K- or Na-promoted catalysts show CO selectivity of 99% at low temperatures which slightly decreases to 97% and 93% at 260 °C, respectively for CuK/C and CuNa/C.

The CO selectivity at a similar conversion level (7.9-11.5 %) is reported in Fig. 10a. More specifically, in Fig. 10a, CO selectivity (%) for the carbon-supported catalysts is presented as a function of temperature at comparable CO₂ conversion level. The CO₂ conversions were 8.9% for Cu/C, 11.5% for CuK/C, and 7.9 % for CuNa/C. The applied conditions were 40 bar(g), 220-240 °C, 700 mL min⁻¹ g_{Cu}⁻¹, 2000 h⁻¹ GHSV, 2.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%. The data reported in Fig. 10a clearly show that K and Na promoters suppress the MeOH formation and the Sabatier reaction. In terms of overall catalytic performance, the addition of Na and especially K to copper-based catalysts was beneficial for enhancing the activity in CO₂ hydrogenation and suppressing almost completely the methanol formation at high pressure.

Second analysis of performances at higher pressures

The performance of the alkali-promoted carbon-supported copper-based catalysts was investigated at higher pressure (40 bar(g) instead of 20 bar(g)) in a temperature range of 200-260 °C. At higher pressures, MeOH formation is more favorable, with a CO selectivity at the thermodynamic equilibrium below 55% over the whole temperature range. However, for industrial applications, it is much more relevant to work at higher pressures, as this decreases the capital investments per unit product. Additionally, the GHSV was halved in comparison to the test at 20 bar(g), making the contact time of reactant gas with the catalytic active sites longer, which also favors MeOH formation over CO. Therefore, testing the catalysts in these conditions allows to really challenge the potential of alkali (K and Na) promoted catalysts in producing CO.

Fig. 9b shows (a) CO₂ conversion (%) and (b) CO selectivity (%) for the carbon-supported catalysts as a function of temperature. The applied conditions were: 40 bar(g), 700 mL min⁻¹ g_{Cu}⁻¹, GHSV 2000 h⁻¹, 2.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%. Thermodynamic

5 CO₂ conversion (%) and CO selectivity (%) were calculated with HSC9 software considering the experimental feed and CO, CH₃OH and CO₂ as carbonaceous species. Fig. 9b, frame a, shows the CO₂ conversion at 40 bar(g) as a function of temperature (200-260 °C). All catalysts show an increase in CO₂ conversion with increasing temperature, as for lower pressures. Fig. 9b, frame b, shows the CO selectivities at 40

10 bar(g). Only traces of CH₄, up to 0.7 % selectivity, were detected. The CO selectivity for the unpromoted Cu/C catalyst is much lower than at 20 bar(g). Thermodynamically, higher pressures enhance the synthesis of methanol. Remarkably, the K- or Na-promoted catalysts retain their very high CO selectivities also at this high pressure and low GHSV: 99% at low temperatures, which slightly decreases to 97% and 93% at 260 °C,

15 respectively for CuK/C and CuNa/C.

The CO selectivities at similar conversion levels (7.5-11.5 %) comparing results from testing at 20 bar(g) and 40 bar(g), are shown in Fig. 10b. More specifically, Fig. 10b shows CO and MeOH selectivity (%) for the carbon-supported catalysts at comparable

20 CO₂ conversion levels at 40 and 20 bar(g). CO₂ conversions at 40 bar(g): 8.9% for Cu/C, 11.5% for CuK/C, 7.9 % for CuNa/C. The applied conditions at 40 bar(g) were: 220-240 °C, 700 mL min⁻¹ g_{Cu}⁻¹, 2000 h⁻¹ GHSV, 2.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%. CO₂ conversions at 20 bar(g): 7.6% for Cu/C, 7.5% for CuK/C, 10.0 % for CuNa/C. The applied conditions at 20 bar(g) were: 220-260 °C, 1400 mL min⁻¹ g_{Cu}⁻¹, 4000 h⁻¹ GHSV, 3.2 mg Cu,

25 H₂/CO₂/He = 67.5/22.5/10 vol%. K and Na promoters suppress the MeOH formation and the CH₄ formation, regardless of the pressure. In general, there is little difference between Na and K promotion, which both enhance the CO₂ conversion and suppress almost completely the methanol formation, also at high pressures and lower GHSV, where methanol synthesis is favored over copper-based catalysts. Without wishing to be bound

30 to theory, the alkali promotional effect is ascribed to the fact that, on the one hand, alkali metals facilitate the CO₂ adsorption and activation due to their inherent basicity and, on the other hand, they mitigate the hydrogenation capacity of Cu, thus inhibiting hydrogenation of reaction intermediates to form CH₄ and CH₃OH. In other words, and again without wishing to be bound to theory, it is assumed that part of the intermediates is

formed on promoter sites instead of Cu surface which hinders the hydrogen access and spatially mitigates the hydrogenation capacity of catalysts, thus inhibiting the formation of CH₄ and CH₃OH.

5 Carbon-supported catalysts' stability

One of the main problems related to Cu-based catalysts is catalyst deactivation by aggregation of supported copper particles. In other words, a challenge for Cu-based catalysts is a potential loss of metal surface area, and hence catalyst activity, due to the growth of the supported copper particles. This is enhanced by the relatively low melting point of copper and by carbon supports due to the relatively weak interaction between metal nanoparticles and carbon materials. Therefore, evaluating the stability of the catalysts is fundamental.

15 First analysis of catalysts' stability

Fig. 11a shows the measurement profile in terms of CO₂ conversion and weight-normalized copper time yield (CTY) for the carbon-supported catalysts as function of TOS at different reaction temperatures. The applied conditions were 40 bar(g), 700 mL min⁻¹ g_{Cu}⁻¹, 2000 h⁻¹ GHSV, 2.2 mg Cu, H₂/CO₂/He = 67.5/22.5/10 vol%. The catalysts show an initial decrease in activity during the first 15 hours on stream, after which the conversion was relatively stable. The stability of the catalysts can be evaluated by comparing the activity of the catalysts at the end of the first isothermal step at 260 °C and when returning to the same reaction conditions after 70 hours (indicated by the arrows in Fig. 11a). The CO₂ conversion decreased from 18% to 17% and from 18% to 16% for the CuK/C and Cu/C catalysts, respectively.

Fig. 12 reports the transmission electron micrographs and particle size distributions for the Cu/C and CuK/C catalysts in the fresh and used state. More specifically, Fig. 12 shows transmission electron micrographs with corresponding particle size distributions of the (a,b,c) Cu/C and the (d,e,f) CuK/C catalysts in the fresh (a,d) and used (c,f) state. The Cu/C catalysts show a more marked change in the particle distribution in comparison to the K-promoted catalyst. The analysis of the TEM images of the used CuK/C evinces the presence of a few large particles in the range of 30-40 nm (not considered in d_s

calculation), which was not observed for the unpromoted catalysts. Fresh and used surface-averaged particle size can be used to calculate the catalysts' turnover frequency (TOF). At 200 °C, the TOF for the Cu/C catalyst was $8.5 \times 10^{-4} \text{ s}^{-1}$ after 46 h on stream considering the initial Cu particle size, and $9.6 \times 10^{-4} \text{ s}^{-1}$ after 85 h on stream considering the used Cu particle size. The K-promoted catalyst shows higher values of TOF both at the beginning and the end of the catalytic test, with values of $3.3 \times 10^{-3} \text{ s}^{-1}$ and $3.5 \times 10^{-3} \text{ s}^{-1}$, respectively. Also at higher temperatures (260 °C), the TOF values of $8.7 \times 10^{-3} \text{ s}^{-1}$ and $9.5 \times 10^{-3} \text{ s}^{-1}$ for the unpromoted catalysts and $1.0 \times 10^{-2} \text{ s}^{-1}$ and $1.1 \times 10^{-2} \text{ s}^{-1}$ for the K-promoted catalysts remained stable comparing 20 h and 70 h on stream. For both catalysts, the TOF values, considering fresh and used particle size, do not change significantly indicating that the loss of active surface area seemed to be the main cause of activity loss.

The above results illustrate the potential of utilizing alkali and alkaline earth metals as promoter metals in Cu/C catalyst for the rWGS reaction. The tested catalysts did not show any undesired side reactions and thus resulted in almost negligible H_2 loss in methane formation, which is a low value product in rWGS reaction.

Second analysis of catalysts' stability

Fig. 11b shows the CO_2 conversion and weight-normalized copper time yield (CTY) versus time on stream at 40 bar(g) pressure and different reaction temperatures. The applied conditions were: 40 bar(g), $700 \text{ mL min}^{-1} \text{ g}_{\text{Cu}}^{-1}$, 2000 h^{-1} GHSV, 2.2 mg Cu, $\text{H}_2/\text{CO}_2/\text{He} = 67.5/22.5/10 \text{ vol\%}$. Thermodynamic CO_2 conversion (%) and CO selectivity (%) were calculated with HSC9 software considering the experimental feed and CO, CH_3OH and CO_2 as carbonaceous species. The catalysts show an initial decrease in activity during the first 15 hours on stream. A stabilization period of a few tens of hours has generally been reported for Cu-based catalysts at high-pressure conditions.

An indication of the stability of the catalysts is a comparison between the activity at the end of the first isothermal step at 200 °C and the activity when returning to the same reaction conditions after 85 h (indicated by the arrows in Fig. 11b). The CO_2 conversion did not change significantly for any of the catalysts, remaining stable at 2% and 6% for the Cu/C and CuK/C catalysts, respectively. For both catalysts only slight particle growth was

observed after catalysis, i.e. the average particle size increased from 7.6 nm to 9 nm for the unpromoted catalyst and from 8.9 nm to 9.7 nm for the K-promoted catalyst. The transmission electron micrographs and particle size distributions for the Cu/C and CuK/C catalysts in the fresh and used state are the same as reported in Fig. 12.

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Based on the results presented herein it is concluded that the use of a weakly interacting carbon support greatly enhanced the Cu-alkali intimacy leading to a threefold increase in the CO₂ conversion, clearly outperforming the tested oxide-supported catalysts. Furthermore, both methanol and methane formation were suppressed, leading to close to 100% CO selectivity, even at a 9:1 H₂:CO₂ ratio and at 40 bar(g) pressure. Furthermore, the carbon-supported catalysts showed no significant activity loss over 100 hours. These results clearly illustrate the advantages of K and Na as a promoter for carbon-supported Cu catalysts for a low temperature reverse-water-gas-shift reaction.

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15 Further disclosure

The present invention further provides the following items:

1. A catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals, wherein the atomic ratio between copper and promotor metal in the catalyst is larger than 1:1.

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2. The catalyst according to item 1, wherein the atomic ratio between copper and promotor metal ranges from $\geq 2:1$ to $\leq 20:1$.

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3. The catalyst according to item 1 or 2, wherein the copper is present in an amount of 1 to 50 wt.%, based on the total weight of the catalyst.

4. The catalyst according to any preceding item, wherein the promotor metal is sodium, potassium, or a combination thereof.

30

5. The catalyst according to any preceding item, wherein the promotor metal is sodium which is present in an amount of 0.05 to 0.60 wt.%, based on the total weight of the catalyst.

6. The catalyst according to anyone of items 1 to 4, wherein the promotor metal is potassium which is present in an amount of 0.20 to 1.00 wt.%, based on the total weight of the catalyst.

5

7. The catalyst according to anyone of items 1 to 3, wherein the promotor metal is magnesium, calcium, strontium, or a combination thereof.

8. The catalyst according to any preceding item, wherein the carbon is selected from layered graphene sheets, carbon nanofibers, carbon nanotubes, graphite and activated carbon.

9. The catalyst according to item 8, wherein the carbon is selected from layered graphene sheets which have a Brunauer–Emmett–Teller surface area of $> 50 \text{ m}^2/\text{g}$.

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10. The catalyst according to item 7 or 8, wherein the carbon is selected from layered graphene sheets which have a total pore volume of 0.70 to $1.10 \text{ cm}^3 \text{ g}^{-1}$.

11. The catalyst according to any preceding item, wherein the copper is at least partially present in metallic form (oxidation state = 0) and the promotor metal is at least partially present in oxidised form (oxidation state > 0).

12. The catalyst according to any preceding item, wherein the catalyst is free of iron.

13. A method of producing carbon monoxide, comprising the steps:

- i) providing a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals, wherein the atomic ratio between copper and promotor metal in the catalyst is larger than 1:1,
- ii) feeding carbon dioxide and hydrogen to the catalyst, and
- iii) converting the carbon dioxide at least partially into carbon monoxide.

14. The method according to item 13, wherein step iii) is carried out at a temperature of $\leq 300^\circ\text{C}$, preferably at a temperature of $\leq 260^\circ\text{C}$.

15. Use of a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals, wherein the atomic ratio between copper and promotor metal in the catalyst is larger than
5 1:1, for catalysing a hydrogenation of CO₂ into CO.

For all the above items, the same preferred embodiments as outlined hereinbefore are also particularly preferred.

CLAIMS

1. A catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$.

2. The catalyst according to claim 1, wherein the atomic ratio between copper and promotor metal ranges from $\geq 7:1$ to $\leq 30:1$.

3. The catalyst according to claim 1 or 2, wherein the copper is present in an amount of 1 to 50 wt.%, based on the total weight of the catalyst.

4. The catalyst according to any preceding claim, wherein the promotor metal is sodium, potassium, or a combination thereof.

5. The catalyst according to any preceding claim, wherein the promotor metal is sodium which is present in an amount of 0.05 to 0.60 wt.%, based on the total weight of the catalyst.

6. The catalyst according to anyone of claims 1 to 4, wherein the promotor metal is potassium which is present in an amount of 0.20 to 1.00 wt.%, based on the total weight of the catalyst.

7. The catalyst according to anyone of claims 1 to 3, wherein the promotor metal is calcium, strontium, or a combination thereof.

8. The catalyst according to any preceding claim, wherein the carbon is selected from layered graphene sheets, carbon nanofibers, carbon nanotubes, graphite and activated carbon.

9. The catalyst according to claim 8, wherein the carbon is selected from layered graphene sheets which have a Brunauer–Emmett–Teller surface area of $> 50 \text{ m}^2/\text{g}$.

10. The catalyst according to claim 8 or 9, wherein the carbon is selected from layered
5 graphene sheets which have a total pore volume of 0.70 to $1.10 \text{ cm}^3 \text{ g}^{-1}$.

11. The catalyst according to any preceding claim, wherein the copper is at least partially present in metallic form (oxidation state = 0) and the promotor metal is at least partially present in oxidised form (oxidation state > 0).

10

12. The catalyst according to any preceding claim, wherein the catalyst is free of iron.

13. A method of producing carbon monoxide, comprising the steps:

- 15
- i) providing a catalyst comprising a copper-promotor metal phase supported on carbon, wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$,
 - ii) feeding carbon dioxide and hydrogen to the catalyst, and
 - iii) converting the carbon dioxide at least partially into carbon monoxide.

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14. The method according to claim 13, wherein step iii) is carried out at a temperature of $\leq 300^\circ\text{C}$, preferably at a temperature of $\leq 260^\circ\text{C}$.

15. Use of a catalyst comprising a copper-promotor metal phase supported on carbon,
25 wherein the promotor metal is selected from alkali metals and alkaline earth metals excluding magnesium, wherein the atomic ratio between copper and promotor metal in the catalyst is $\geq 7:1$, for catalysing a hydrogenation of CO_2 into CO .

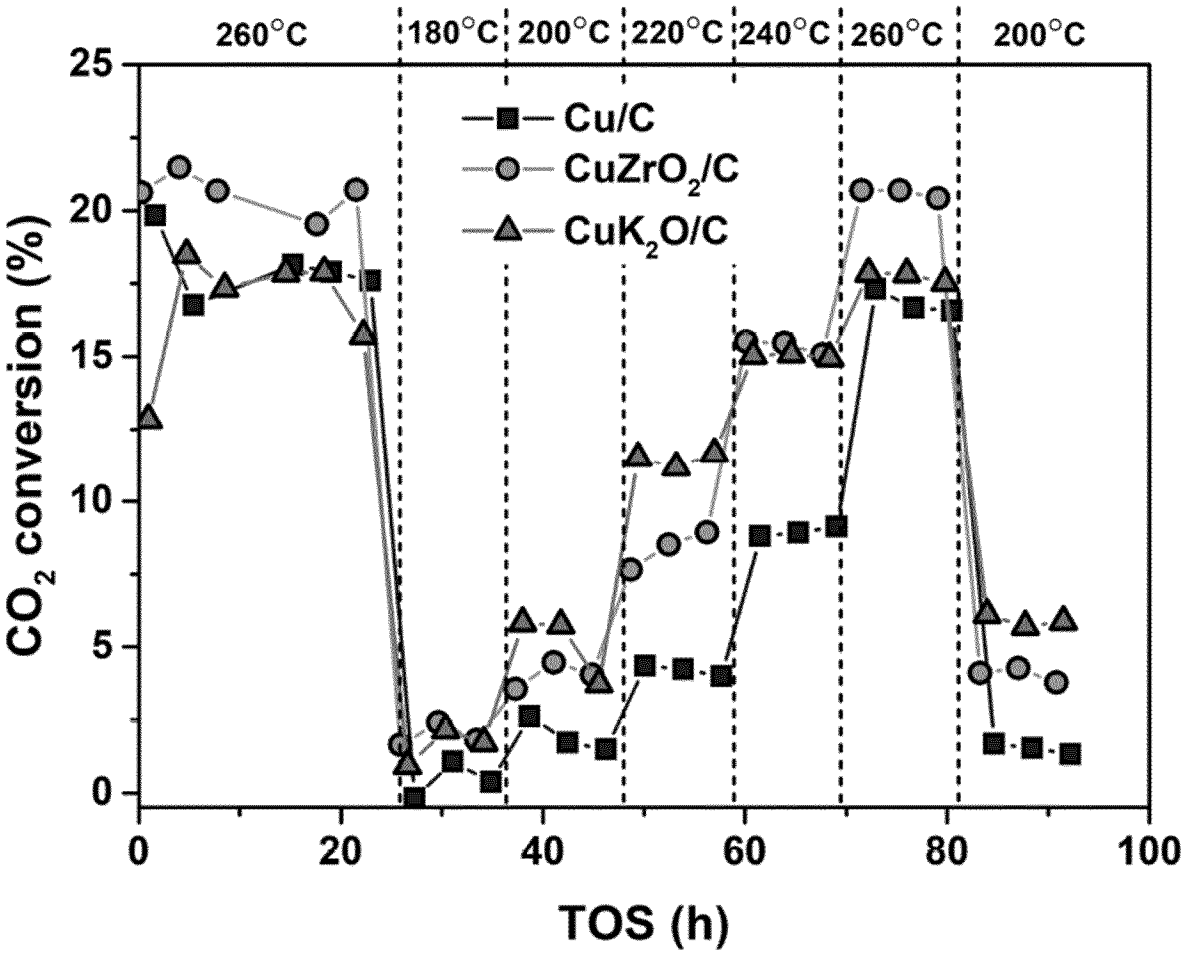


Fig. 1

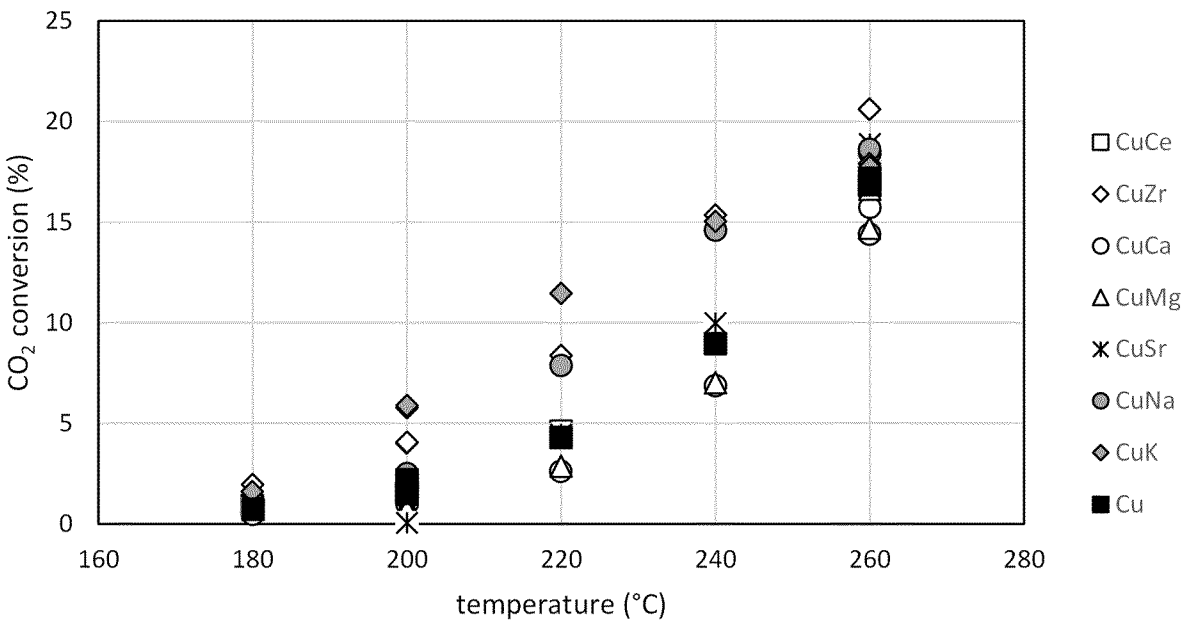


Fig. 2a

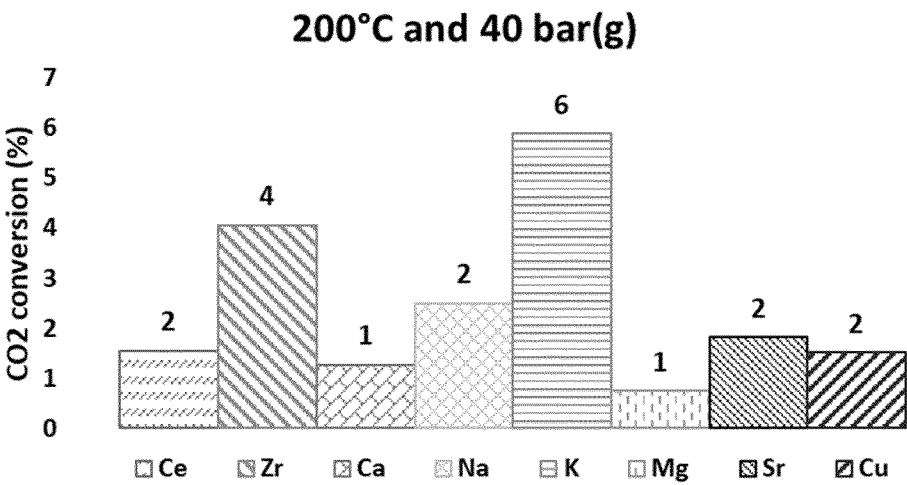


Fig. 2b

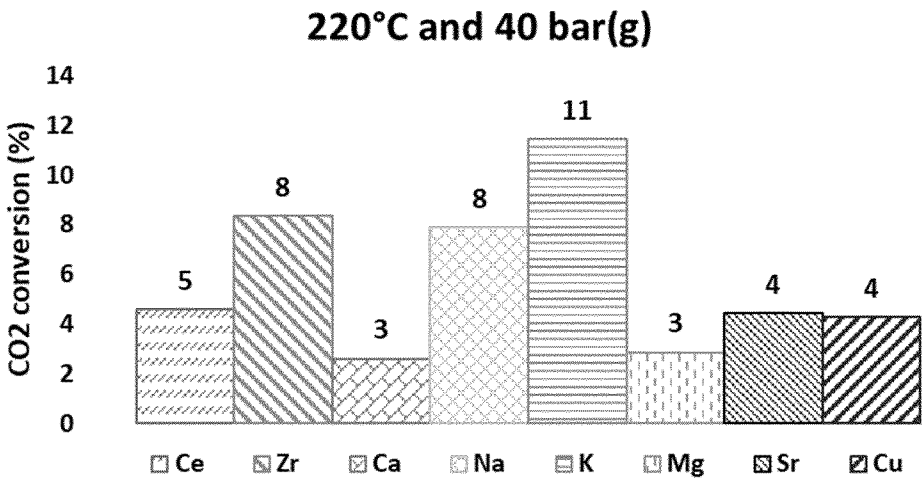


Fig. 2c

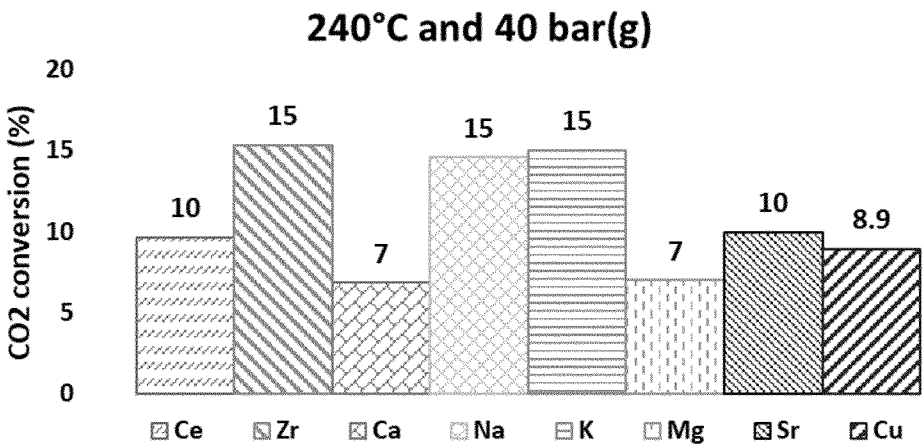


Fig. 2d

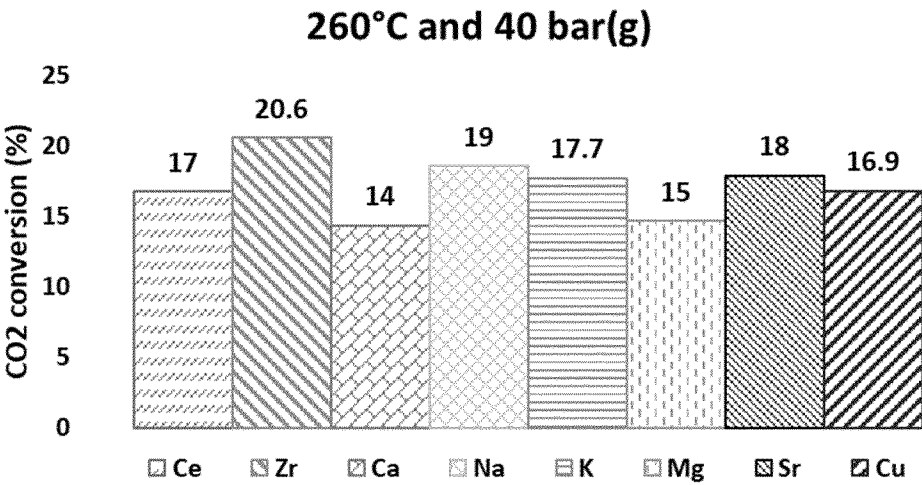


Fig. 2e

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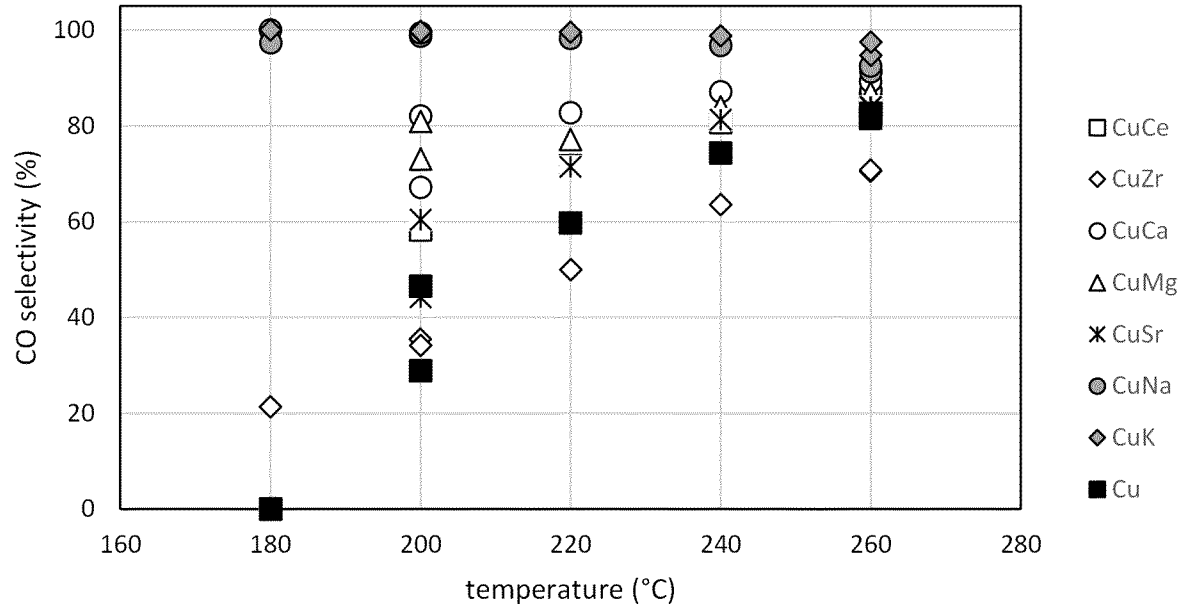


Fig. 3a

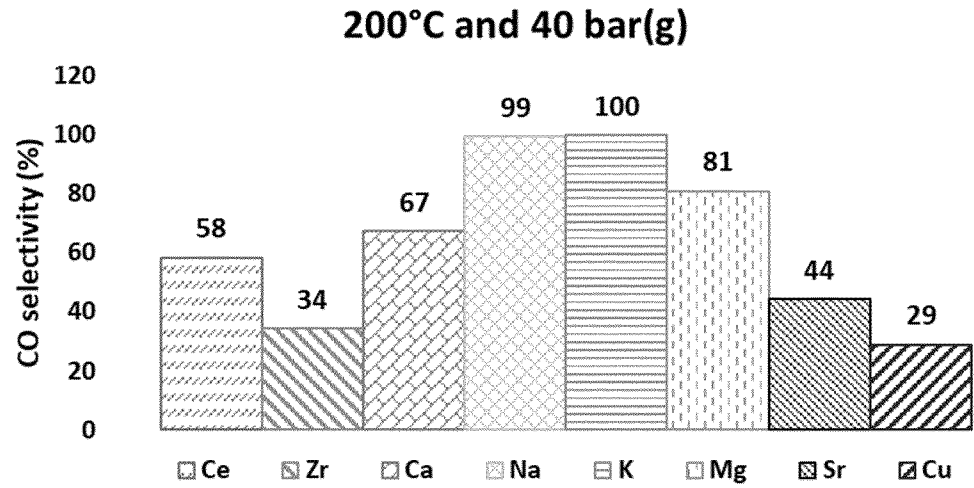


Fig. 3b

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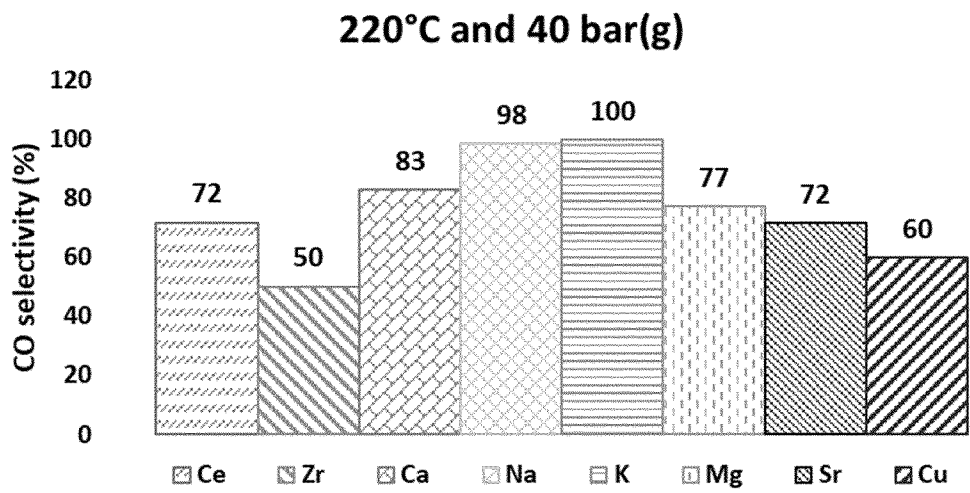


Fig. 3c

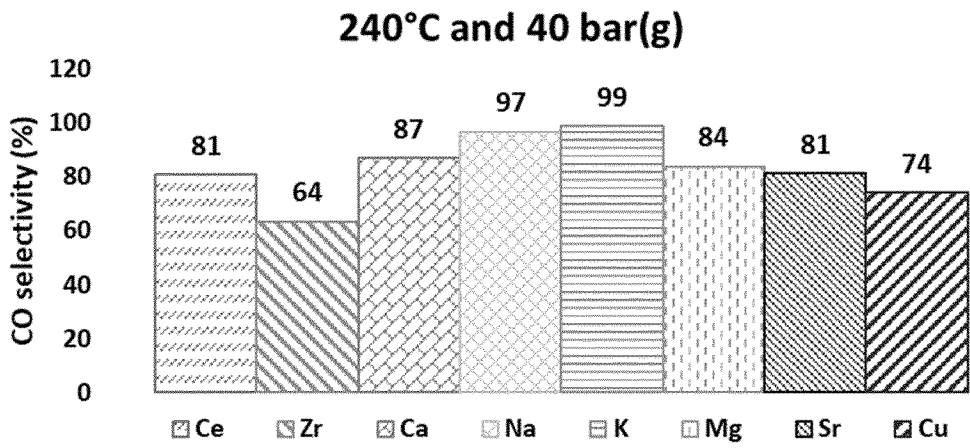


Fig. 3d

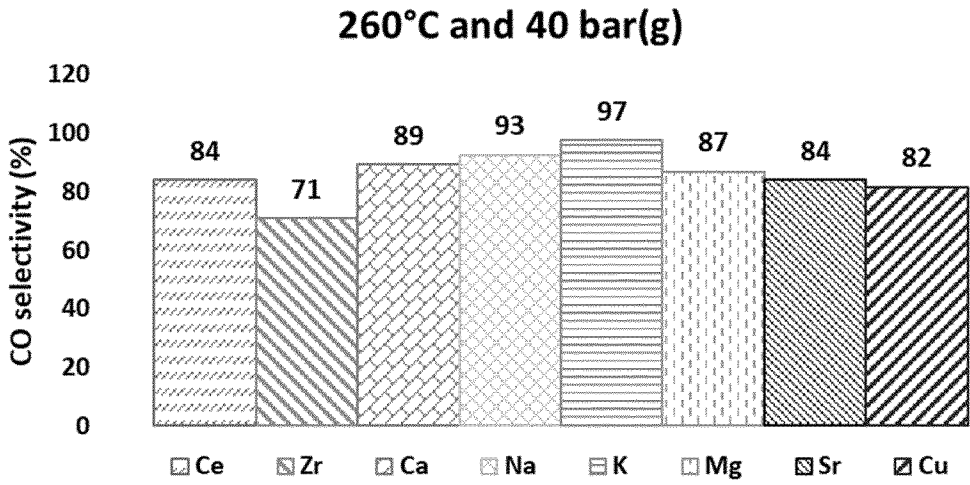


Fig. 3e

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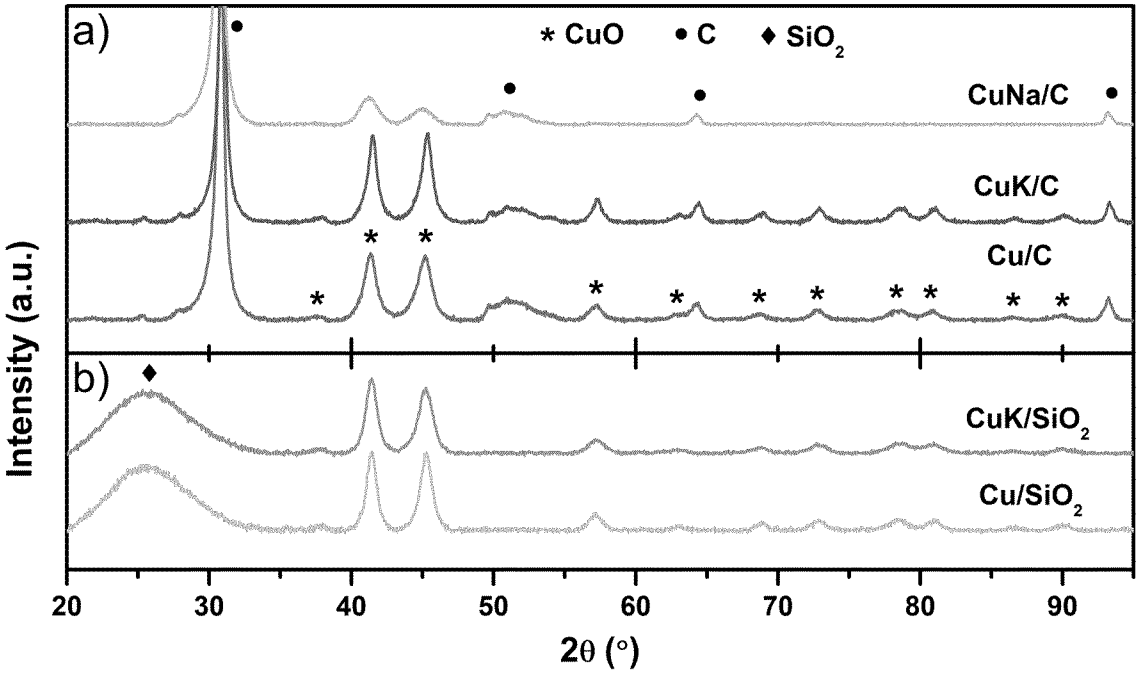


Fig. 4a

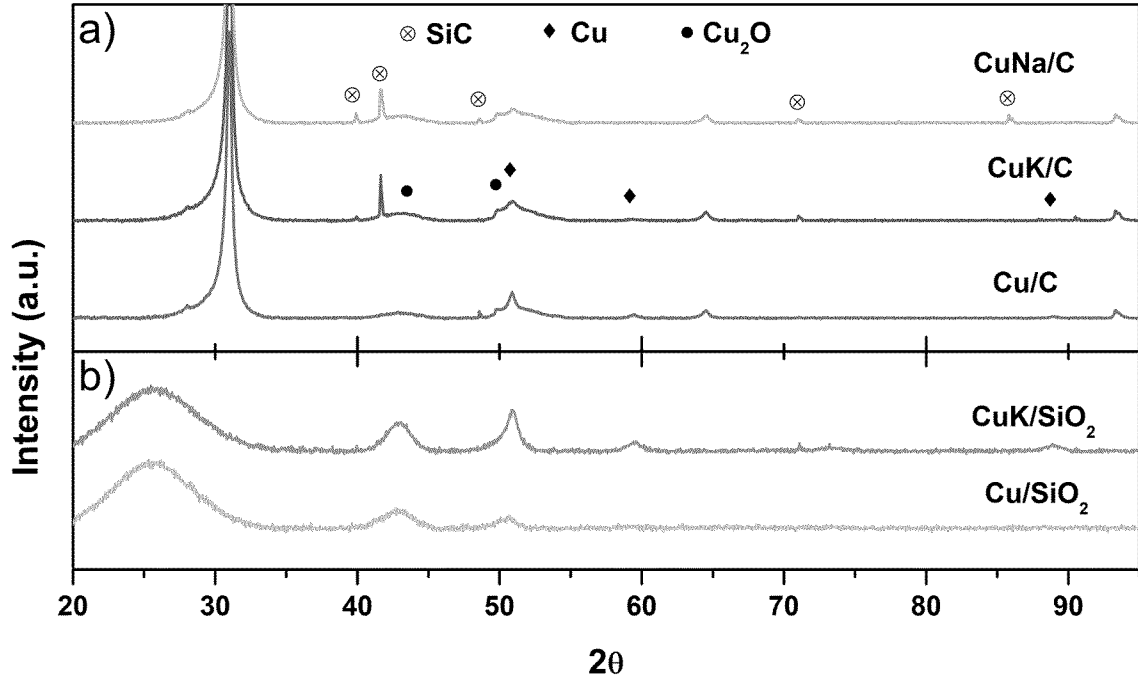


Fig. 4b

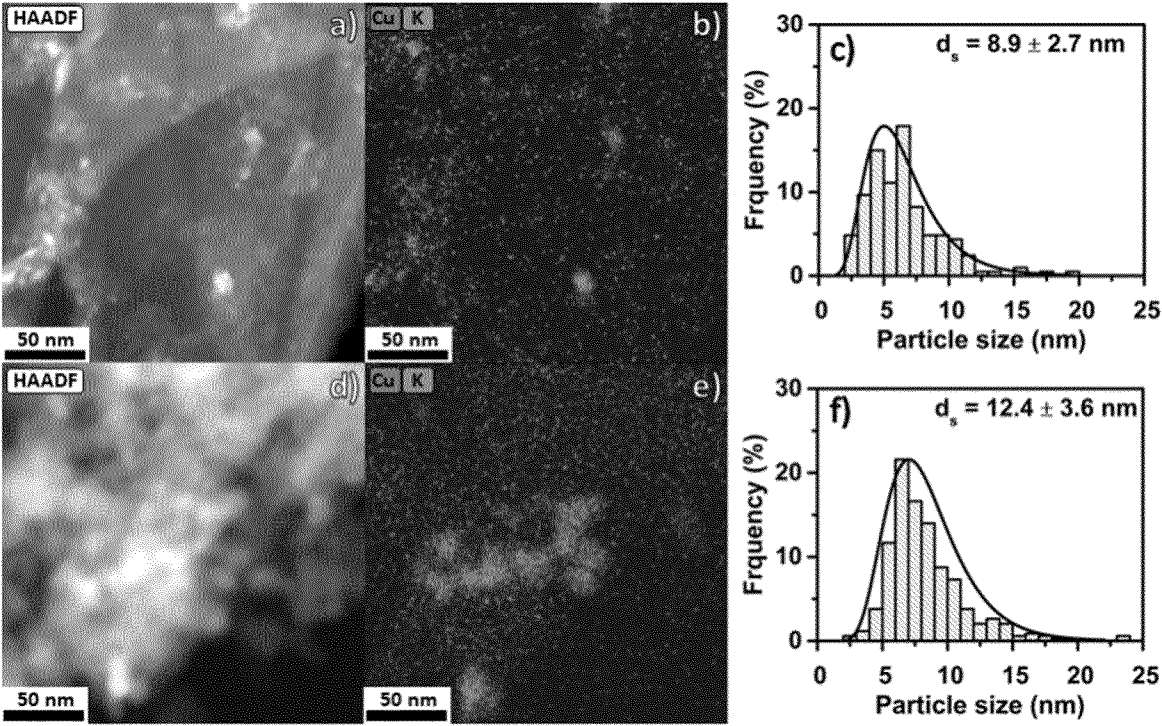


Fig. 5a

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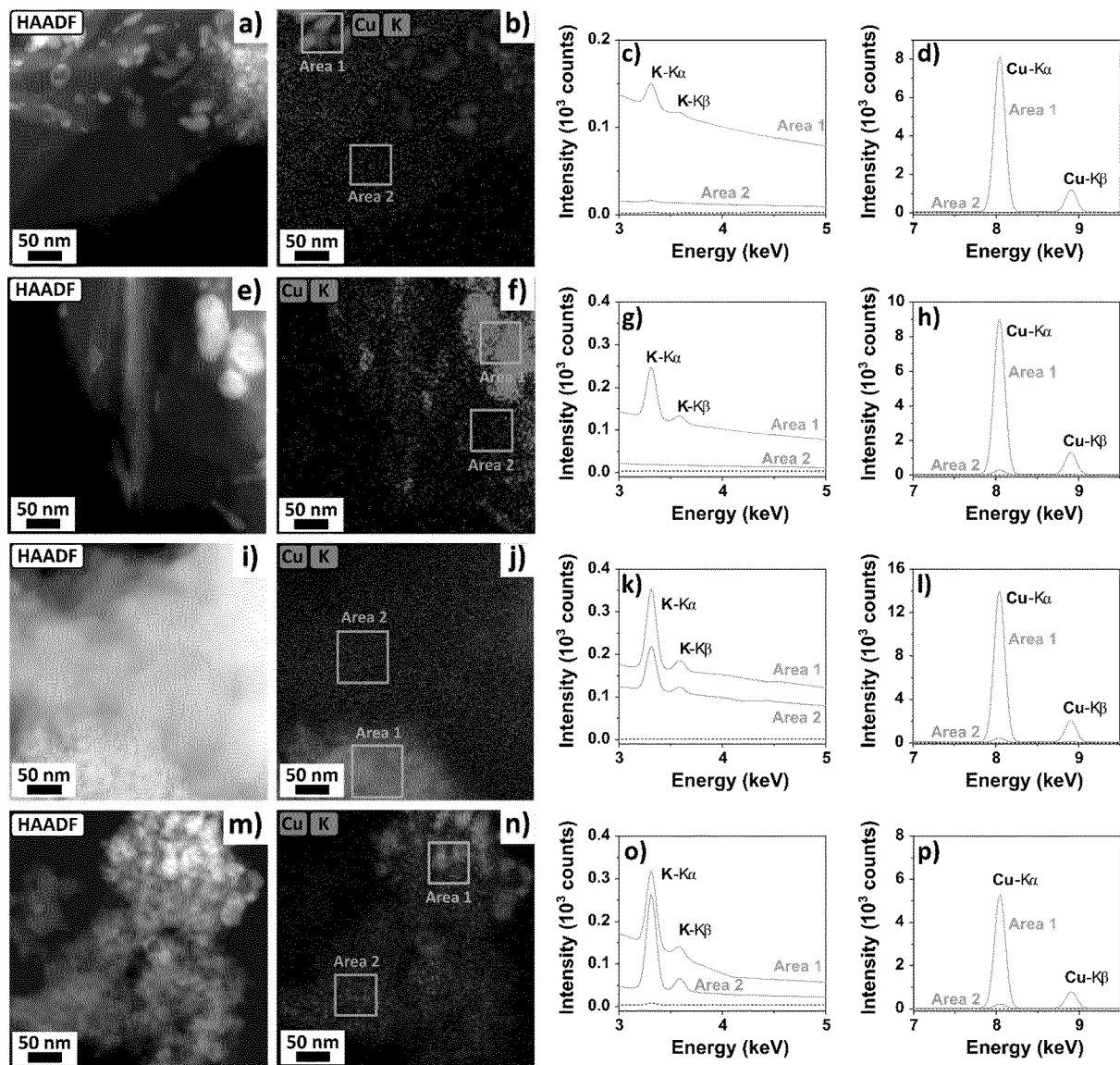


Fig. 5b

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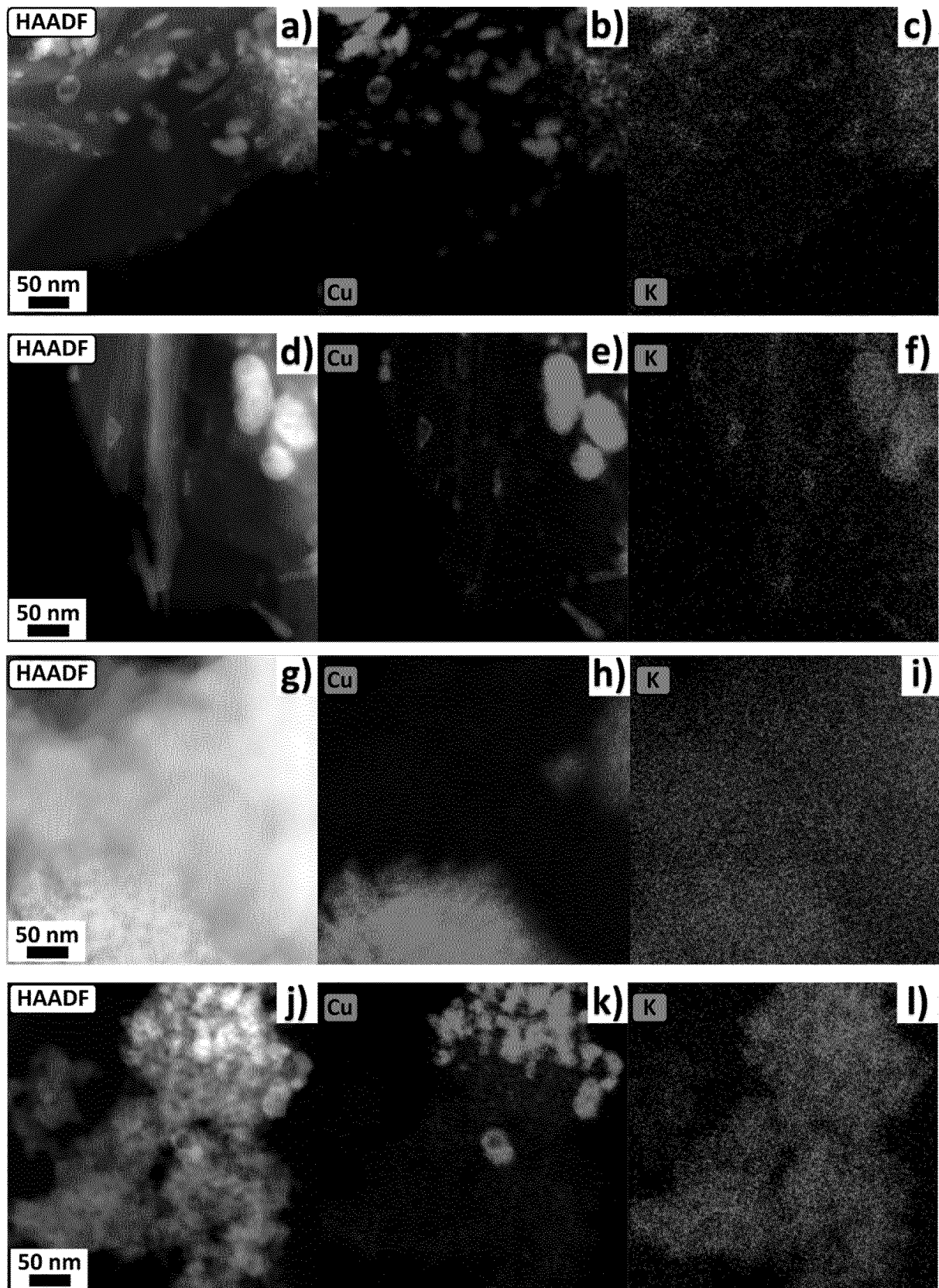


Fig. 5c

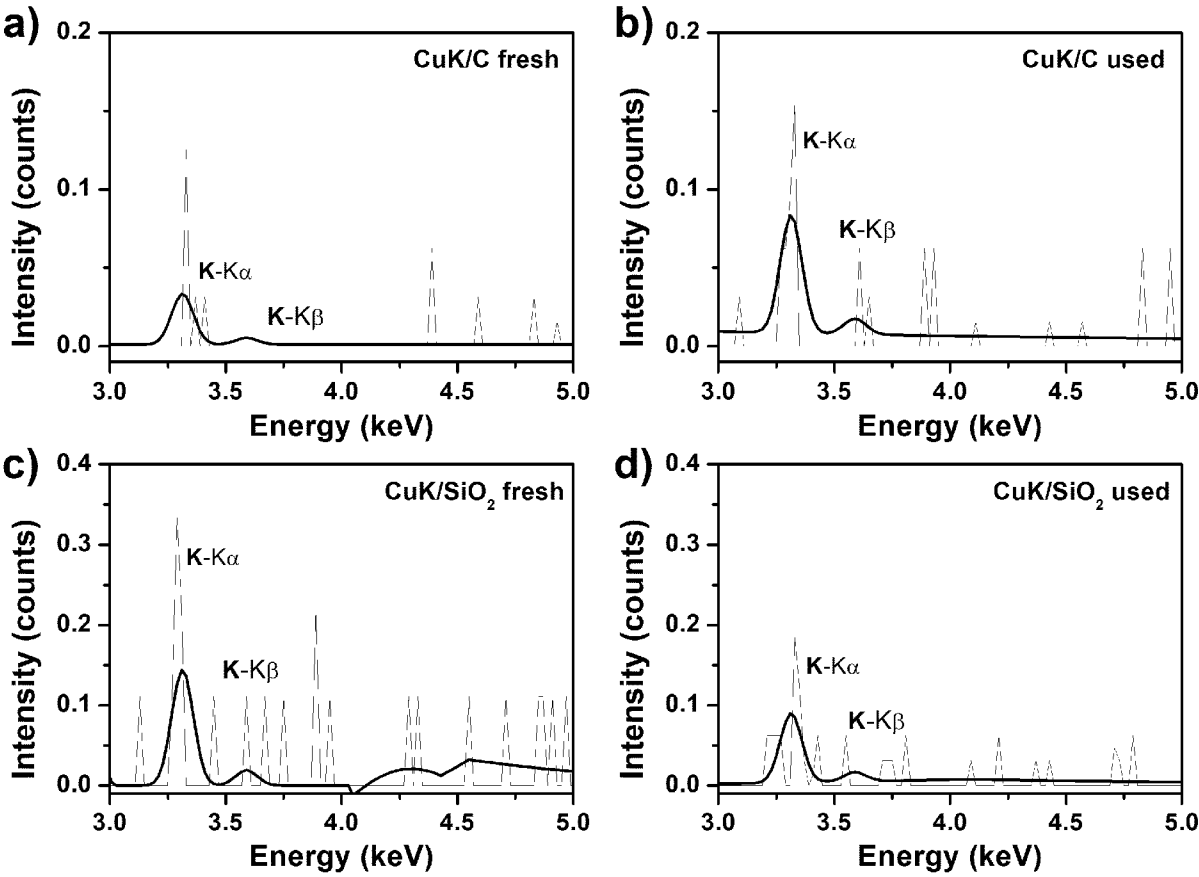


Fig. 5d

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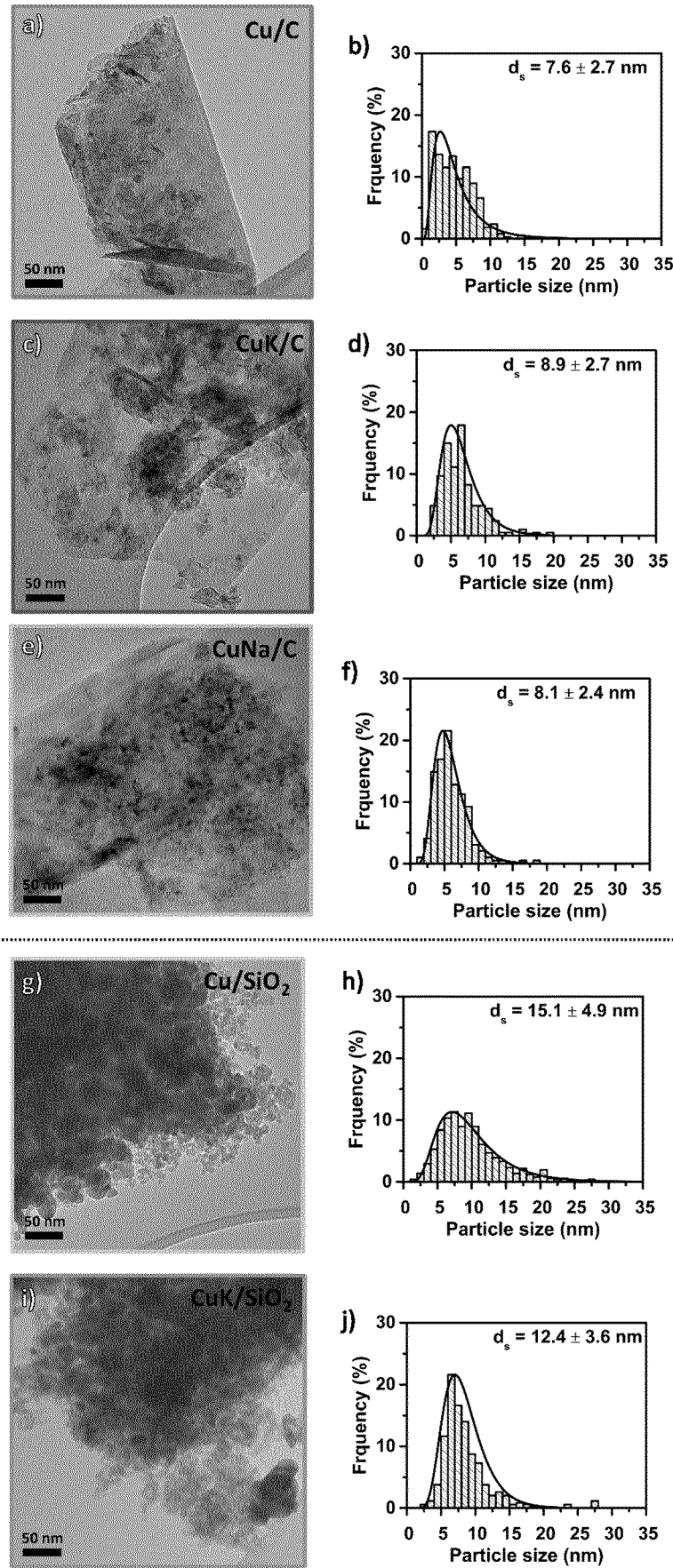


Fig. 5e

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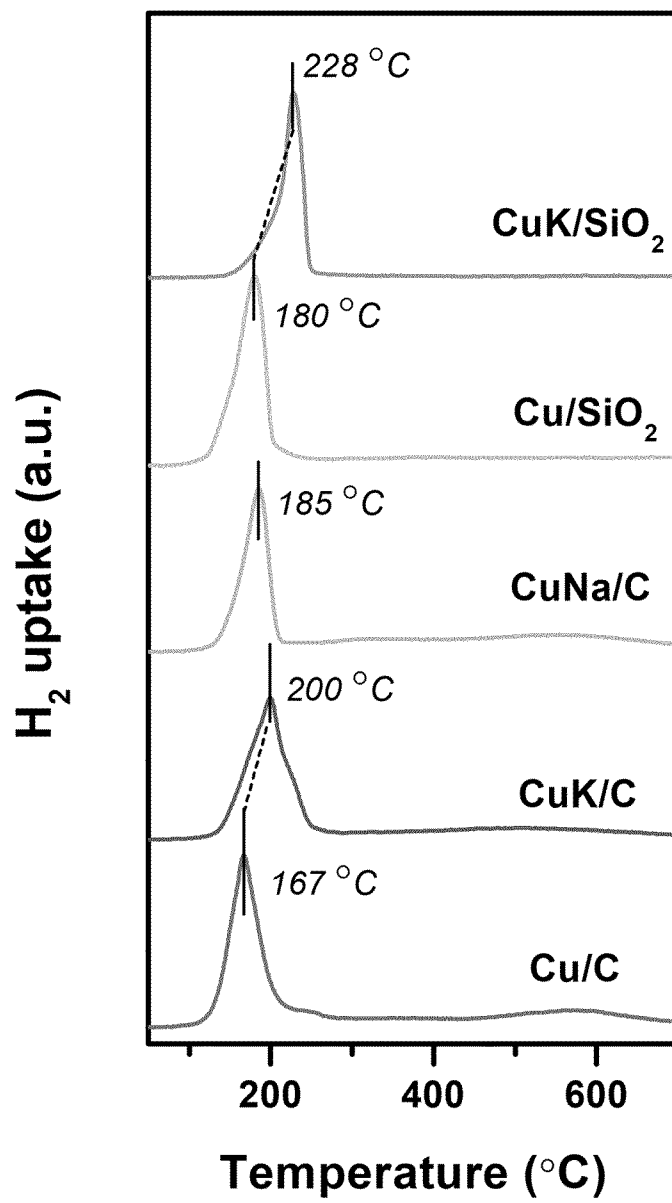


Fig. 6

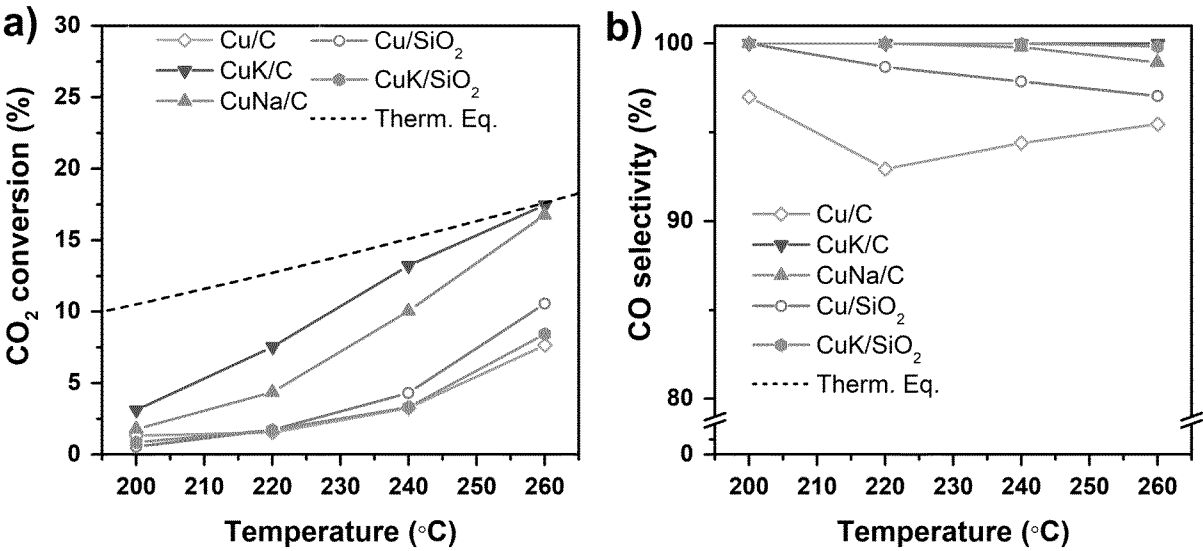


Fig. 7a

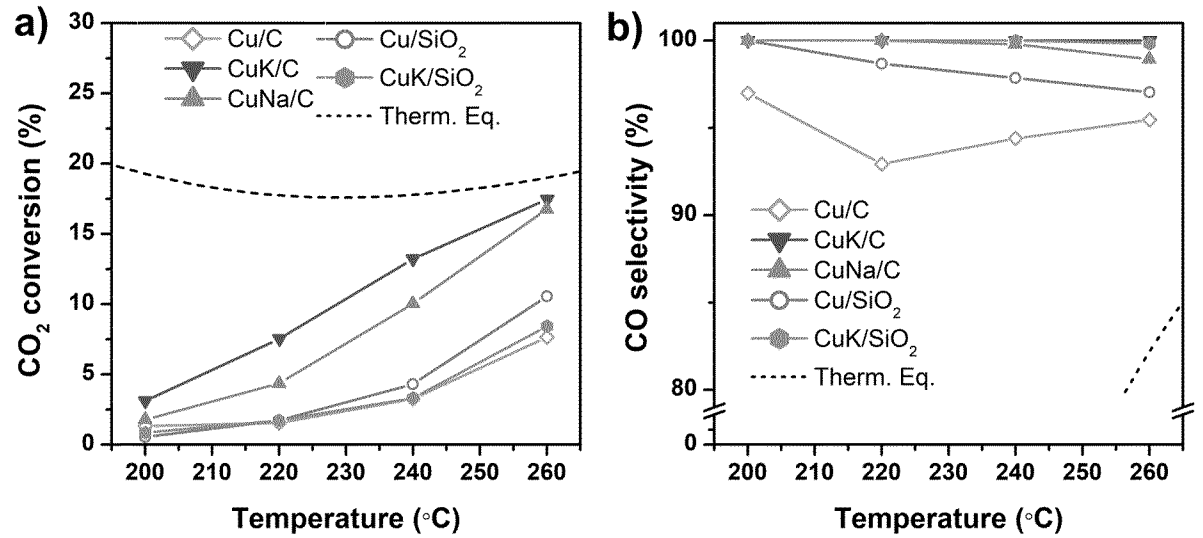


Fig. 7b

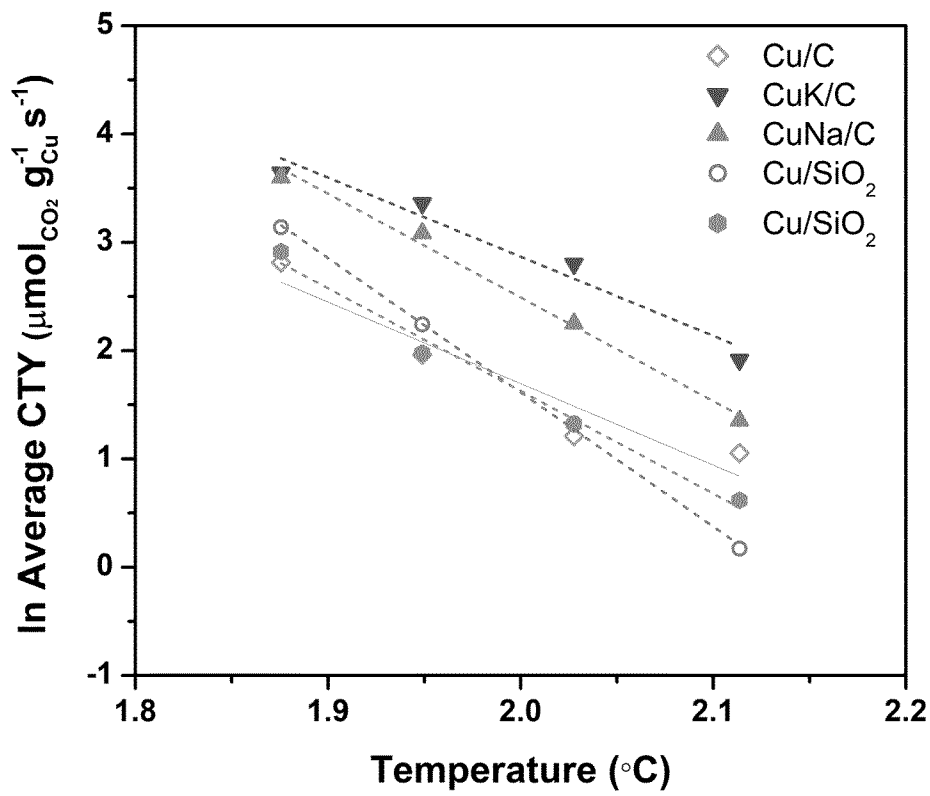


Fig. 7c

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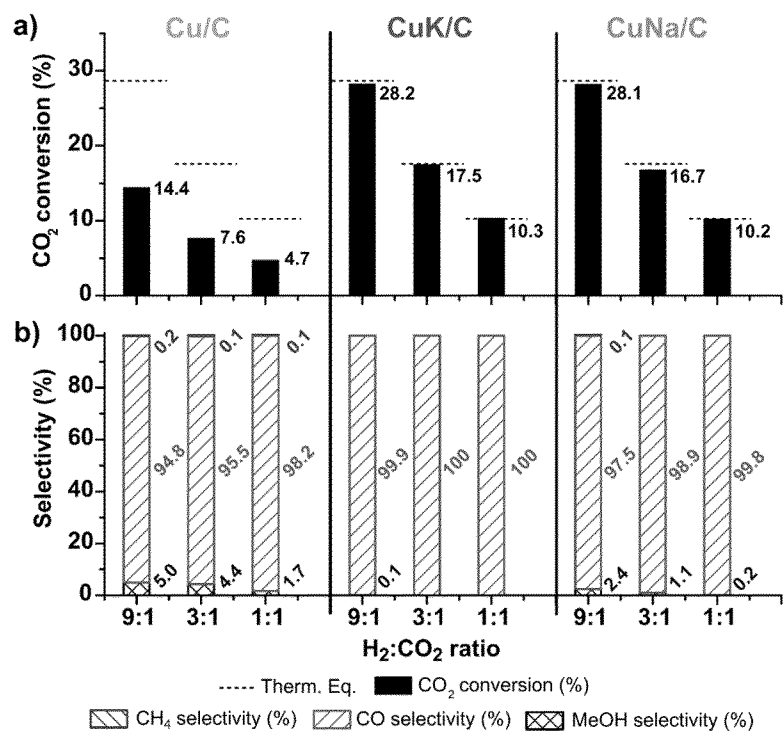


Fig. 8a

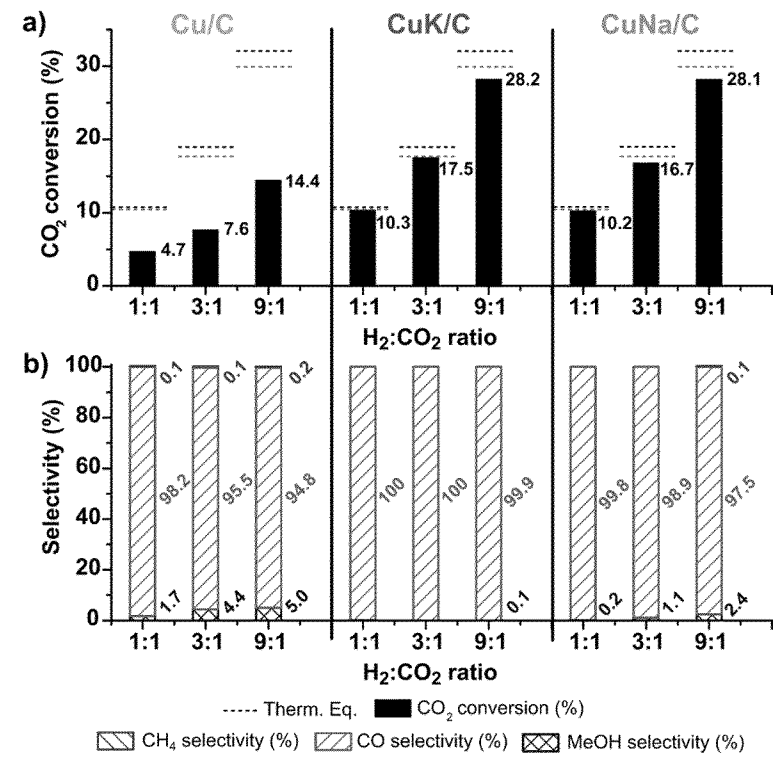
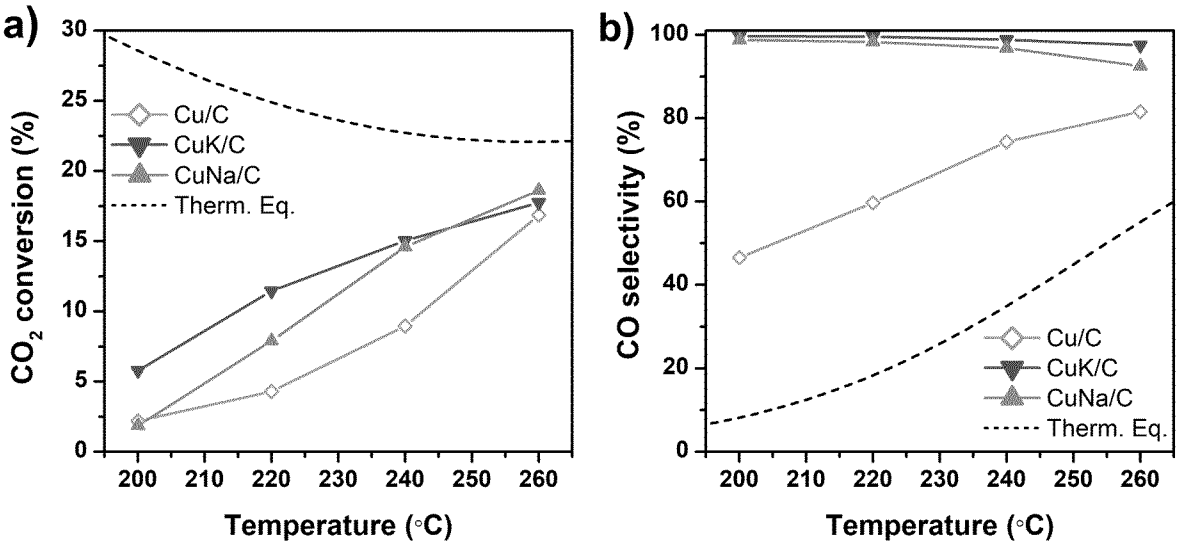
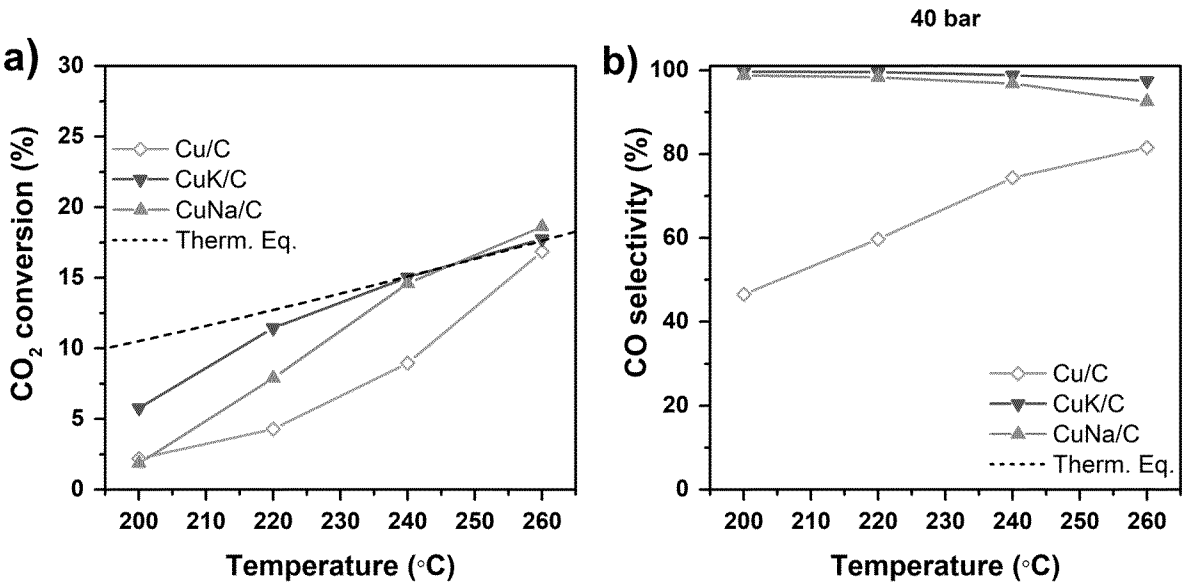


Fig. 8b



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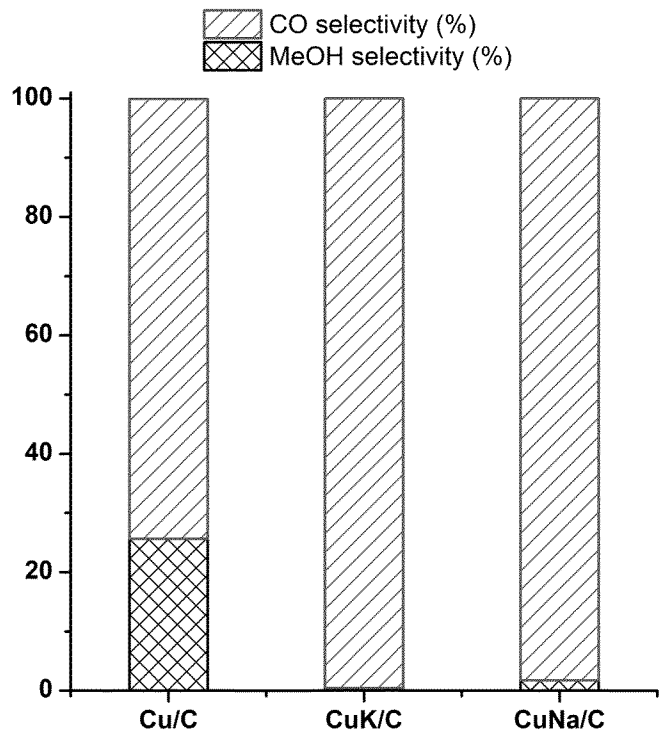


Fig. 10a

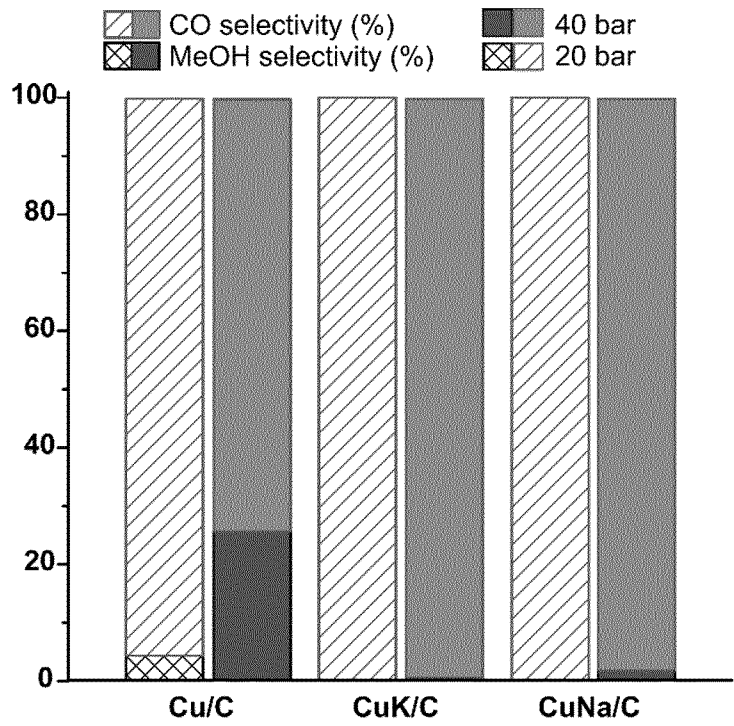


Fig. 10b

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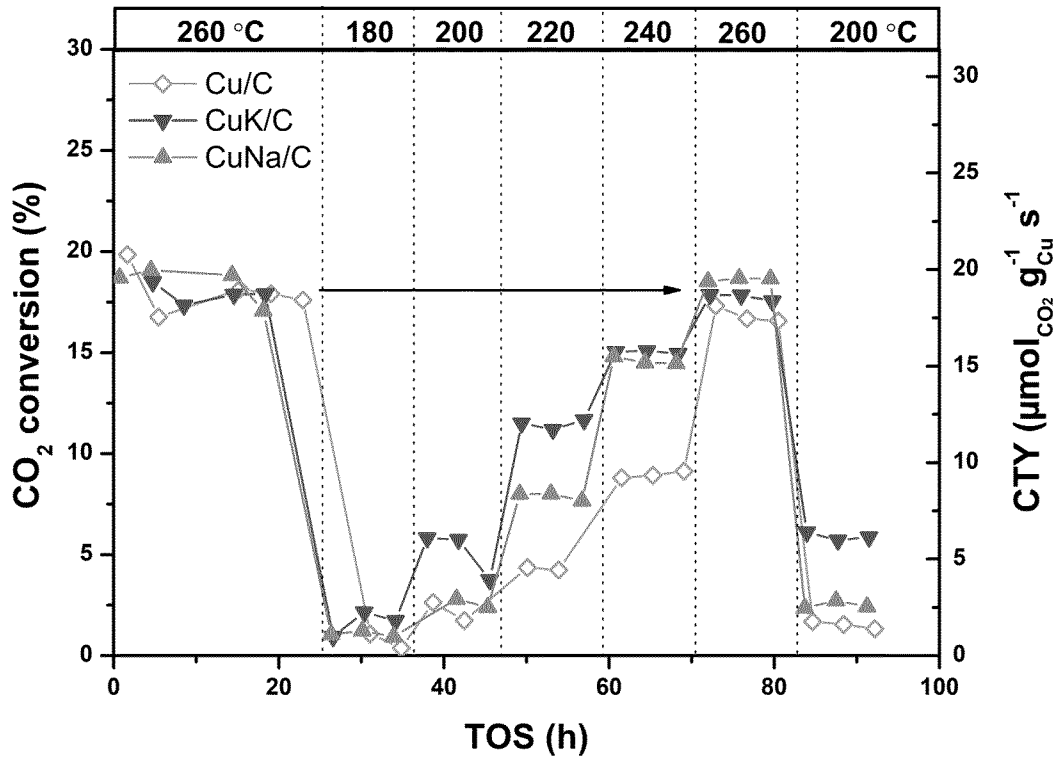


Fig. 11a

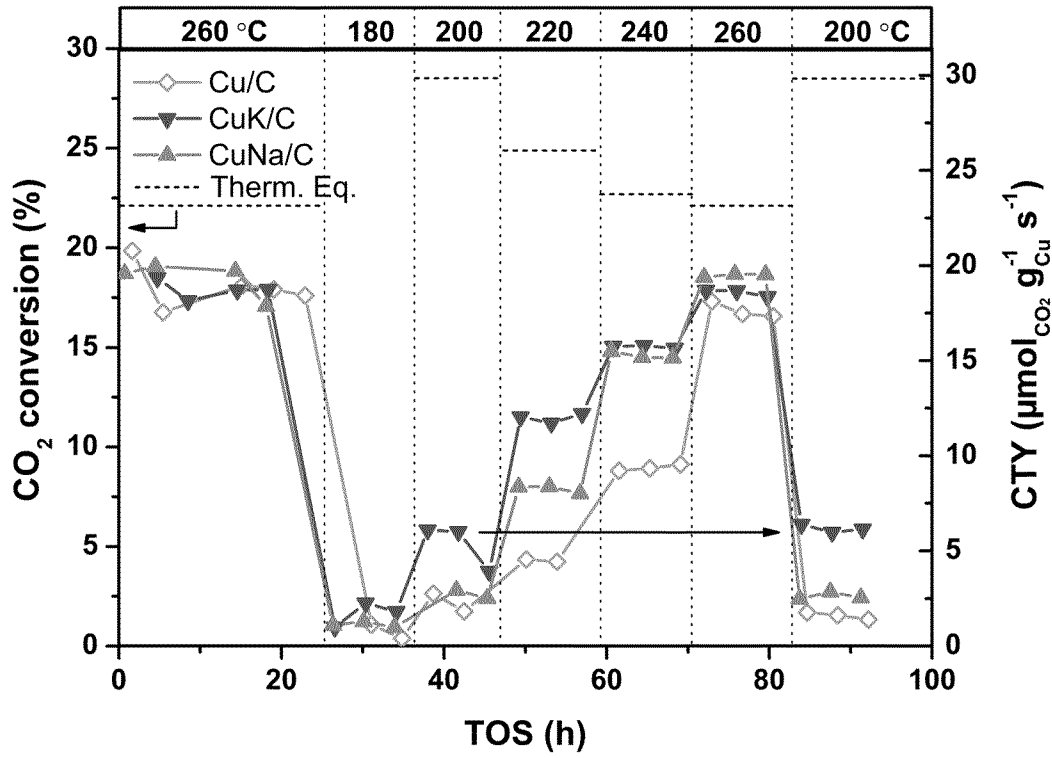


Fig. 11b

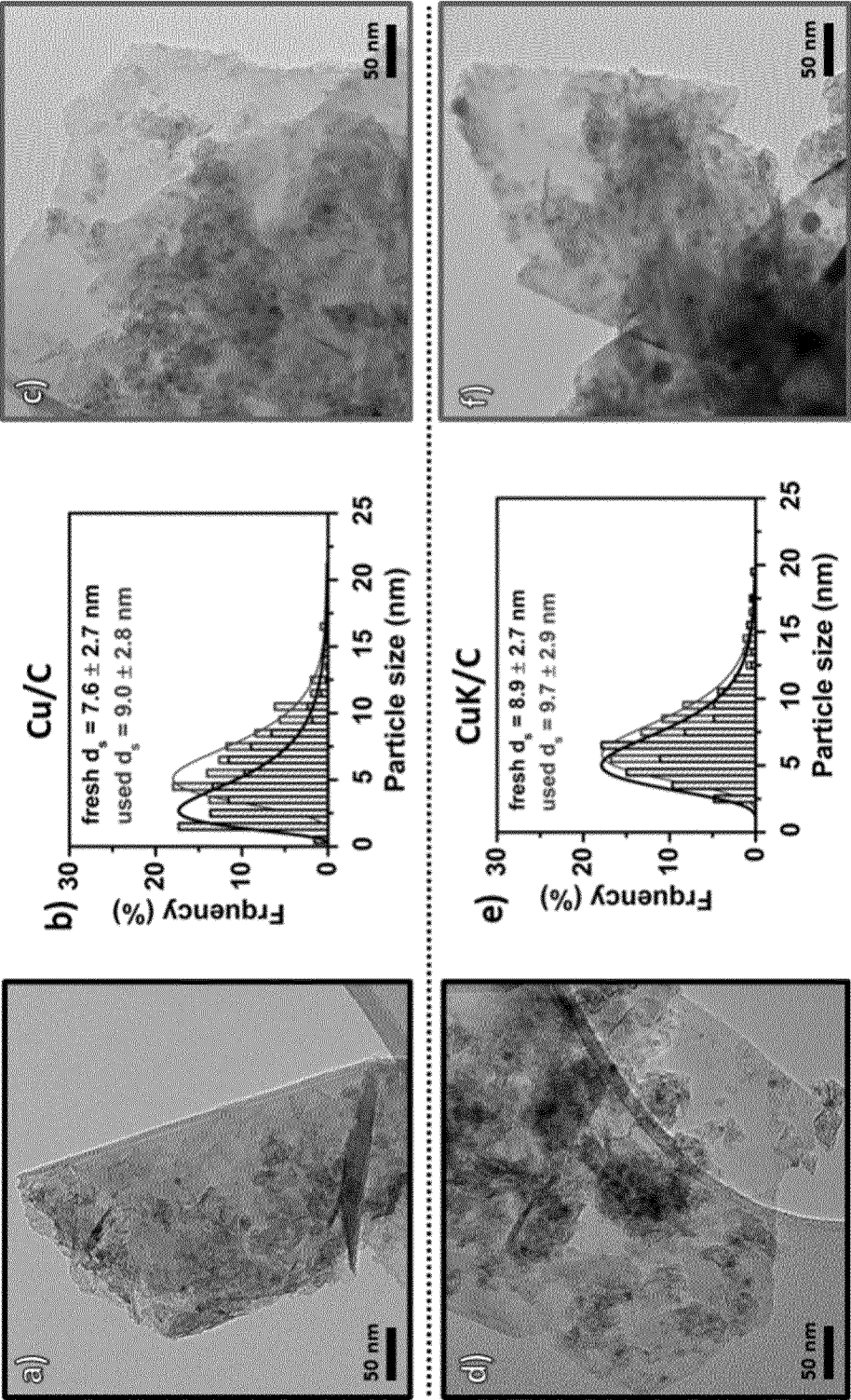


Fig. 12

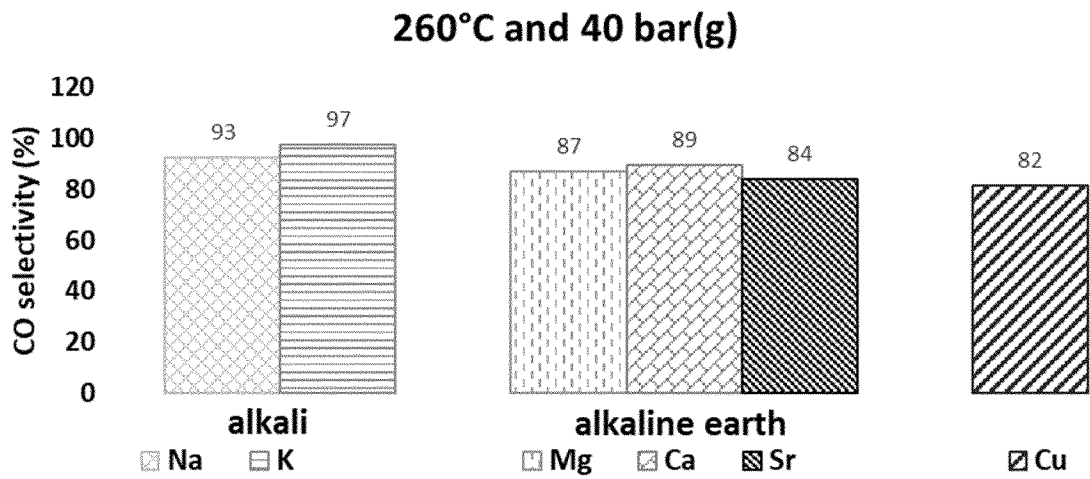


Fig. 13

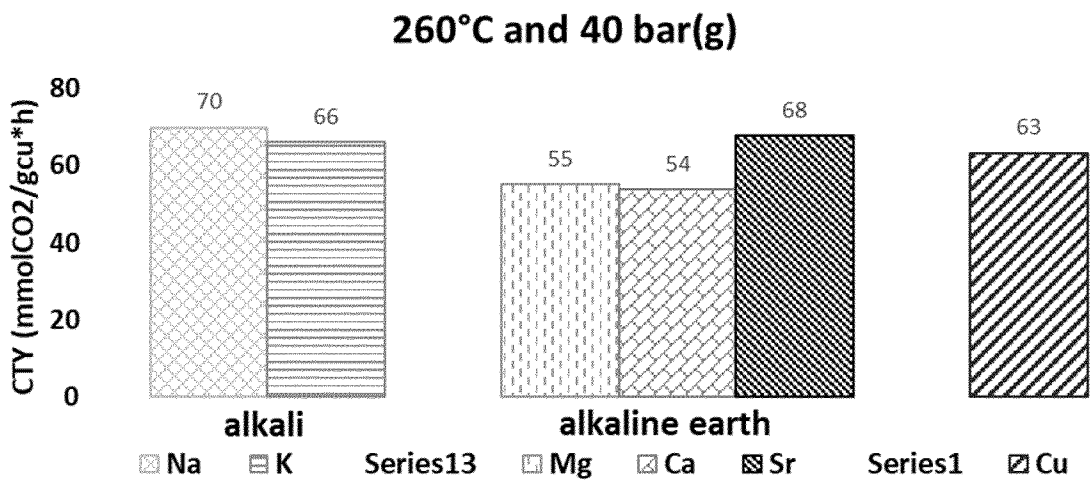


Fig. 14

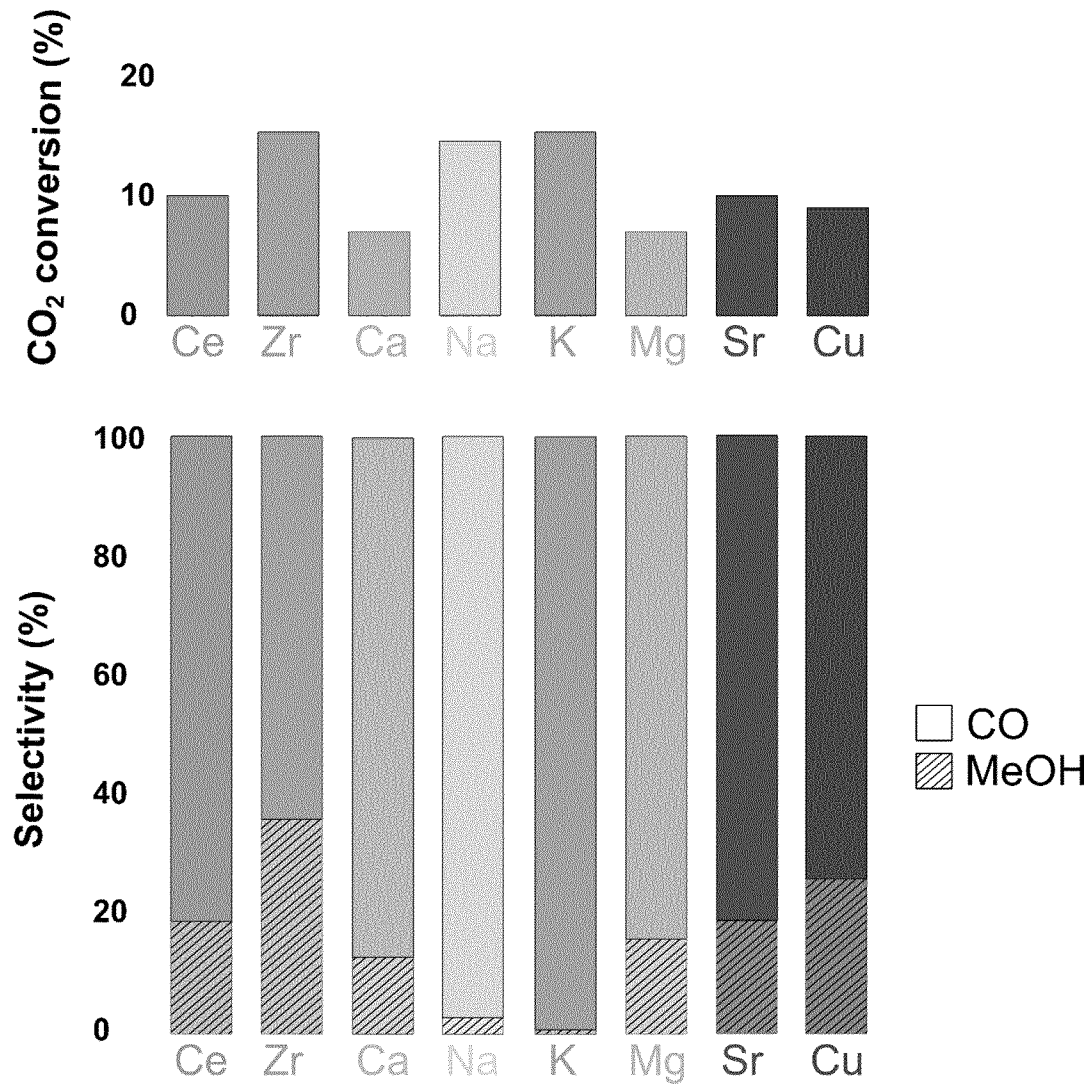


Fig. 15

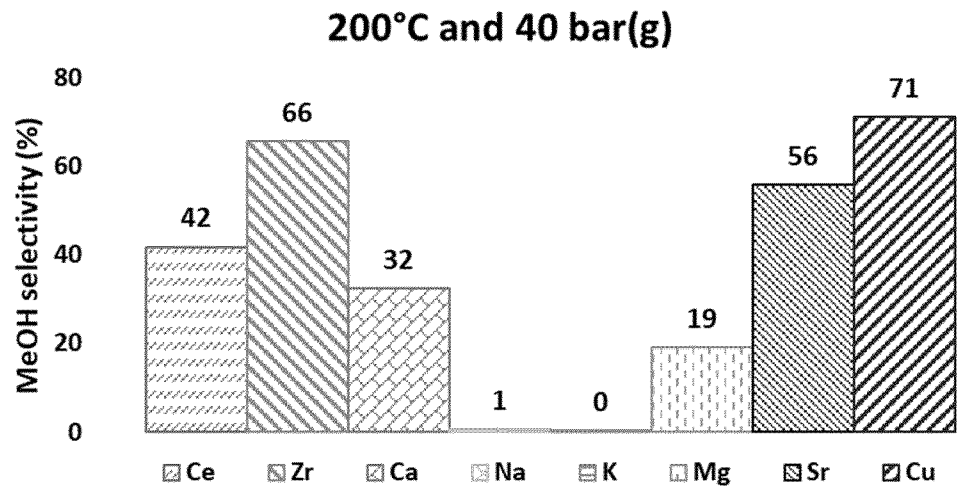


Fig. 16a

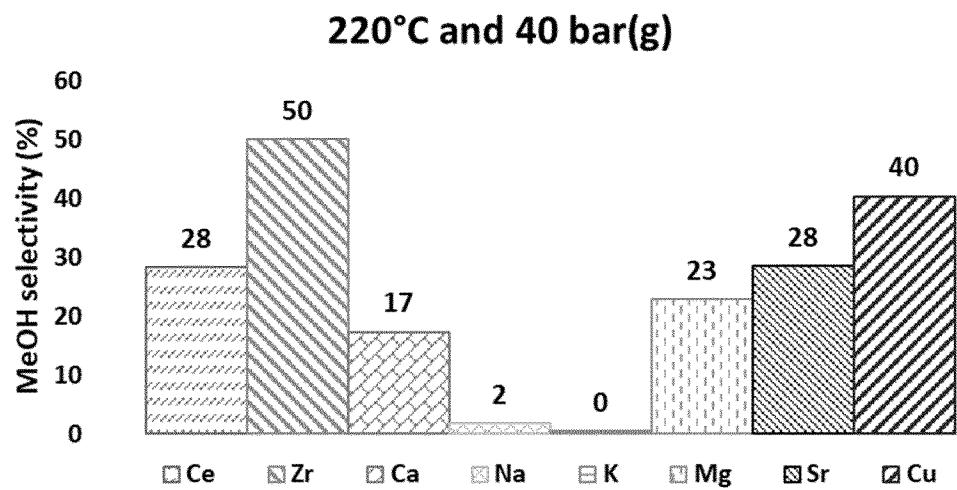


Fig. 16b

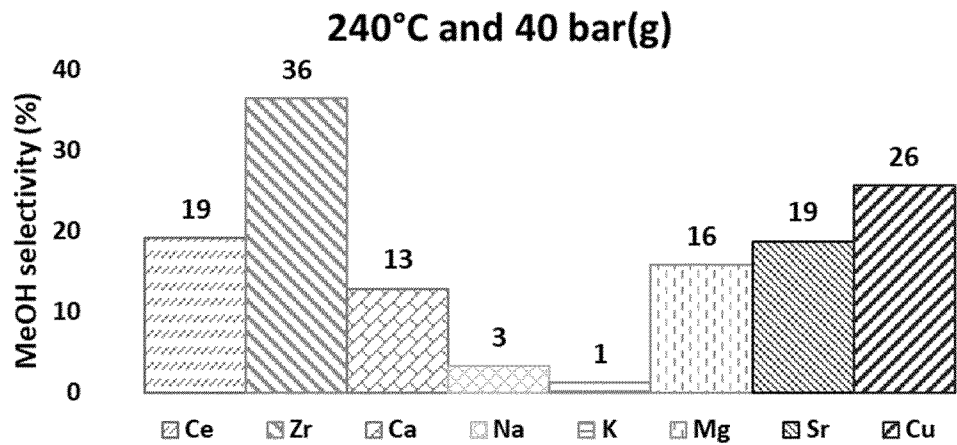


Fig. 16c

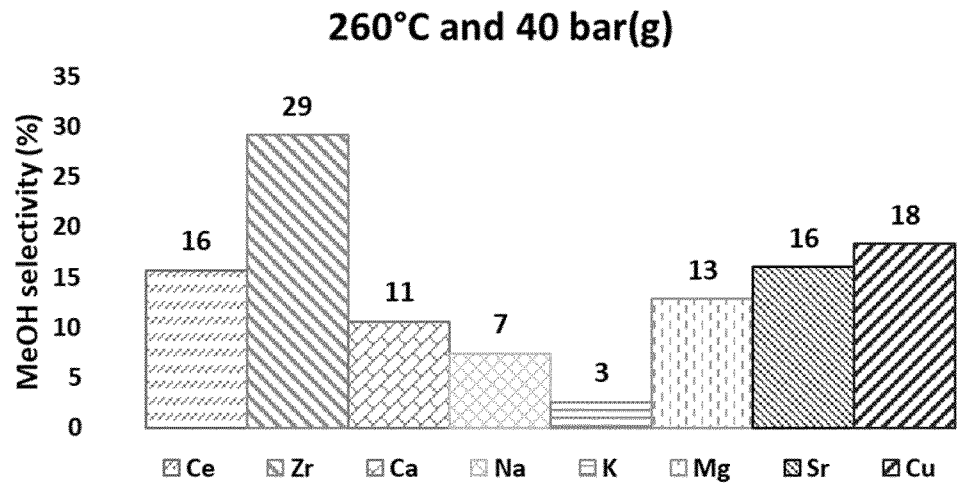


Fig. 16d

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/065271

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	B01J21/18	B01J23/78	B01J35/00	B01J37/02	C01B32/40
	B01J35/40	B01J37/00	B01J37/14		
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 C01B					
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					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
A	WO 2014/116341 A1 (DOW CORNING [US]) 31 July 2014 (2014-07-31) paragraph [0029]				1 - 15
A	US 8 785 343 B2 (LIU JINGWEI [CN]; LI ZEZHUANG [CN] ET AL.) 22 July 2014 (2014-07-22) example 22				1 - 15
A	US 2023/150823 A1 (SCHUETZLE DENNIS [US] ET AL) 18 May 2023 (2023-05-18) table 2				1 - 15
A	US 2022/111361 A1 (NATESAKHAWAT SITTICHA [US] ET AL) 14 April 2022 (2022-04-14) paragraph [0089]				1 - 15
☐ Further documents are listed in the continuation of Box C.					
☒ See patent family annex.					
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"A" document defining the general state of the art which is not considered to be of particular relevance			"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		
"E" earlier application or patent but published on or after the international filing date			"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		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)			"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 such documents, such combination being obvious to a person skilled in the art		
"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search			Date of mailing of the international search report		
29 July 2024			07/08/2024		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Zieba, Roman		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/065271

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2022111361 A1	14-04-2022	EP 3911437 A1	24-11-2021
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		WO 2020150129 A1	23-07-2020