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CuOx/CeO₂ catalyst derived from Metal Organic Framework for Reverse Water-Gas Shift Reaction

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Graphical abstract

Highlights

- An alternative route using a MOF as catalyst precursor has been studied
- The MOF called Cu-BTC has been used as precursor
- The MOF was impregnated with cerium precursor
- The impregnated MOF was pyrolyzed to obtain the catalyst
- With the pyrolysis method we could control the final properties of the catalysts

ABSTRACT:

Herein, we have studied an alternative route for preparing CuO_x/CeO₂ catalysts using metal organic frameworks (MOFs) as precursors. Usually, CuO_x/CeO₂ materials are prepared by wet impregnation of ceria support. In this study, we have impregnated a Cu-MOF with a ceria precursor and then pyrolyzed the impregnated MOF using different conditions and procedures. The prepared catalysts have been characterized by using a wide range of techniques such as XRD, XPS, Raman, and TPR. We have found that the pyrolysis method determines the dispersion of the oxidized copper species on the ceria surface what, in turn, controls the catalytic activity and selectivity of the catalysts in the reverse water-gas shift (RWGS) reaction. We have compared the behavior of the MOF-derived

catalysts against an optimized catalyst prepared by a conventional method (wet impregnation), finding that the MOF-derived catalyst shows better catalytic performance.

KEYWORDS: Metal organic framework, RWGS, Ceria, copper oxide

INTRODUCTION

CO₂ is one of the most dominating greenhouse gases, which mainly comes from fossil fuels (coal, natural gas and oil) combustion for energy generation, transportation and chemical industry.[1] The utilization of CO₂ for the production of chemicals is one of the proposed ways to mitigate the global warming, by which CO₂ is used as a cheap, nontoxic and abundant C1 source. Conversion of CO₂ to CO through the Reverse Water-Gas Shift (RWGS) reaction (Equation. 1) is one of the studied processes for CO₂ utilization to obtain CO which, together with H₂, can be used to produce valuable chemicals via the Fischer-Tropsch reaction.[2]

However, CO₂ reduction is highly endothermic and it requires high operation temperatures. Noble metals-based catalysts can be used for this reaction but, due to their high cost and limited natural abundance, the finding of an alternative catalytic materials is highly requested. Copper-based catalysts have been the most studied catalytic systems for the WGS reaction, and they have also been applied to the RWGS reaction.[3] Liu *et al.* developed a series of Cu-Ni/ γ -Al₂O₃ bimetallic catalysts for CO₂ hydrogenation. They studied the effect of the Ni/Cu ratio on conversion and selectivity, and founded that Cu favors CO formation, meanwhile Ni favors CH₄ formation.[4] However, the main problem of Cu-based catalysts is their poor thermal stability; at high temperatures, copper nanoparticles sinter and the catalyst deactivates. This fact can be avoided by adding a thermal stabilizer. For example, the addition of a small amount of iron effectively improves the catalytic activity and stability of Cu/SiO₂ catalysts at high temperature.[5]

An usual approach in heterogeneous catalysis to avoid particles sinterization is the use of supports (as SiO₂, ZnO, TiO₂, CeO₂ and γ -Al₂O₃) in order to increase the active phase dispersion (textural promotor) and/or acting as chemical promoters, increasing selectivity and/or conversion.[6] In this sense, CuO_x/CeO₂ has been proposed as a promising system for RWGS. The preparation of CuO_x/CeO₂ catalysts is far for being trivial. It is well known and demonstrated by Martinez-Arias *et al.*[7,8] that the catalytic activity of this system depends on the contact of both ceria and copper species. Copper and ceria are prompt to sinter at temperatures about 400 °C, that is the temperature commonly used for catalysts calcination. For this reason, the preparation of CuO_x/CeO₂ catalysts made out from CuO_x nanoparticles and CeO₂ oxide nanoparticles is of great interest.

The use of Metal-Organic Frameworks (MOFs) as precursors of metal catalysts is a relatively new field of research that worth being explored for the preparation of highly dispersed supported active phases. MOFs are coordination compounds based on metallic ions or clusters connected with organic linkers by coordination bonds and other weak interactions, creating three-dimensional networks.[9,10] Due to their interesting properties (large pore surface area, highly designable pore shape and pore size, high dispersion of its components, hybrid characteristics and structural flexibility) they have a wide range of applications.[11,12] Foremost among them are included gas separation and storage[13,14] and heterogeneous catalysis[14]. MOFs have been proved to act as heterogeneous catalysts because (i) the framework itself can act as a catalyst, in which case, metallic centers or pseudo-organic linkers (like porphyrin [11]) are responsible of the catalytic activity, (ii) they can act as host materials for supporting catalysts[15,16] and (iii) they can act as precursors of catalysts by framework decomposition, which is a new way to use MOFs as catalysts.[17] During the thermal decomposition process the metal ions in the MOFs are transformed into metallic or metal oxide nanoparticles and the organic linkers form carbonaceous structures, that can act as a support and facilitate the active phase dispersion.[18]

MOFs can be considered optimum precursors for catalysts preparation, decreasing the problems related to achieve good active phase dispersion. The MOF denominated $\text{Cu}_3(\text{BTC})_2$, or HKUST-1, is one of the most extensively studied copper-based MOFs as catalyst precursor since it was synthesized by Chui *et al.* in 1999[19]. $\text{Cu}_3(\text{BTC})_2$ has a structure constituted by clusters of two copper ions coordinated with four carboxylate groups of organic linkers, generating paddle-wheel building blocks. In this structure, each copper ion of the building block is coordinated with one water molecule, which can be removed or exchanged by other ligands easily.[20] Thermal treatment of this MOF has been studied in several works. Thus, calcination in air produces microporous CuO materials with different architectures[21], decomposition in inert atmosphere leads to symmetrical coraloid Cu 3D superstructures[22] and a combination of both thermal treatments has also been studied.[22][23]

In our approach, we will use a MOF as copper precursor. The precursor of the copper species is not impregnated on a support as traditionally, but the support is impregnated on the MOF, which already contains the copper. CeO_2 is used in this work due to its interesting properties: it is a partially reducible oxide (oxidation states +4 and +3 and has highly mobile oxygen atoms. The oxygen storage capacity (OSC) is the most attractive characteristic of this oxide; it is able to store and supply active oxygen depending on the conditions.[24][25] Thus, through the use of a copper-based MOF as metallic precursor and of CeO_2 as final support/promoter, it is intended to prepare a stable and active catalyst in the RWGS reaction.

EXPERIMENTAL

Catalysts with different atomic percentage of copper and cerium (Table 1) were prepared in two steps. The first one was the impregnation of the MOF (Basolite ® C 300) with a cerium precursor ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\geq 99.99\%$, Aldrich) in methanol (MeOH, 99.98%, Aldrich), with a ratio of 10 mL/g_{solid}. The slurry formed was stirred during 24 h under He bubbling until dryness. The second step consisted in the decomposition of the prepared materials using different methodologies and conditions. For the catalysts, the decomposition was carried out in a laboratory-scale pilot plant provided with a steel reactor, able to work at pressures between 0.1 and 1.5 MPa under different atmospheres (air, nitrogen, helium). Samples were introduced in a pyrex glass tube of 6.5 cm diameter and 21 cm height, which was fit in the steel reactor. Thermal treatments were carried out in a fluidized sand bath, since the heat transfer is very fast and it avoids large temperature gradients. Two decomposition methods were studied in this system:

- 1) Pyrolysis (P): the reactor, loaded with the sample (10 g), was introduced in a fluidized sand bath heated at 550 °C. Once the thermocouple of the inner part (controlling the sample temperature) of the reactor reached the desired temperature (550 °C), the sample were kept in the fluidized sand bath for an hour.
- 2) Flash pyrolysis (Pf): the reactor, loaded with the sample (10 g), was introduced in a fluidized sand bath heated at 550 °C. Once the thermocouple of the inner part of the reactor reached the desired temperature (550 °C), the reactor was removed from the fluidized sand bath.

The samples were prepared using different conditions and compositions (Cu/Ce ratios). The labeling and experimental details are summarized in Table 1.

Table 1. Catalyst composition and experimental conditions of the pyrolysis treatments.

Catalyst	Composition, molar %		Decomposition method	Atmosphere	Pressure, bar
	Cu	Ce			

P ₂₀₋₈₀ (N ₂ , 1bar)	20	80	Pyrolysis	N ₂	1
P ₄₀₋₆₀ (N ₂ , 1bar)	40	60	Pyrolysis	N ₂	1
Pf ₂₀₋₈₀ (N ₂ , 1bar)	20	80	Flash Pyrolysis	N ₂	1
Pf ₄₀₋₆₀ (N ₂ , 1bar)	40	60	Flash Pyrolysis	N ₂	1
Pf ₂₀₋₈₀ (Air, 1bar)	20	80	Flash Pyrolysis	Air	1

It is important for the readers to know that in the first test we did, we used a glass plug flow reactor and it burst during the decomposition of the impregnated precursors.

In order to compare our catalyst with a reference material we have also prepared a catalyst based on previously reported works [26–28]. The ceria support was prepared as follow: 13 g of Ce(NO₃)₃·9H₂O (Aldrich, 99%) and 8 g of urea (Fluka, 98%) were dissolved in 400 ml of ultra-pure water. The mixture was heated at 90 °C with constant stirring for 11 h. Finally, 12 ml ammonia solution (Panreac, 30%) was added drop-wise to ensure complete precipitation. The solid was separated by filtration, washed with ultrapure water, and finally dried at 110 °C overnight. The powder sample was calcined in air at 500 °C for 4 h, using a rate of 3 °C·min⁻¹. The ceria support was impregnated with an aqueous solution of Cu(NO₃)₂·3H₂O (Panreac, 99.999%) with the appropriate concentration to achieve 4 and 8 wt.% Cu loading. Then, catalysts were dried at 90 °C overnight and calcined in air at 500 °C for 4 h, with a heating rate of 3 °C·min⁻¹.

Thermogravimetric experiments were carried out in a Mettler Toledo TGA/SDTA, located in the Research Technical Services of the University of Alicante (SSTTI). An alumina crucible containing 10 mg of sample was heated under 50 ml·min⁻¹ air flow up to 625 °C, at a heating rate of 10 °C·min⁻¹.

XPS spectra were collected using a Thermo Scientific K-ALPHA with Al-K radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot with a diameter of 400 µm, at 3 mA × 12 kV when charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to selectively measure the particular elements.

An estimation of the intensities was done after a calculation of each peak integral, S-shaped background subtraction and fitting the experimental curve to a combination of a Lorentzian (30%) and Gaussian (70%) lines.[29] Binding energies (BE), referenced to the C 1s line at 284.6 eV, have an accuracy of ± 0.2 eV. Before the analysis, catalysts were pre-treated under a reducing atmosphere (flowing 50 ml·min⁻¹ of hydrogen) at 250 °C and then immersed in octane, which was evaporated under vacuum conditions.

Catalysts reducibility was studied with temperature-programmed reduction experiments in a mass spectrometer (Pfeiffer, OmniStar GSD 301), under a mixture of 5% H₂/He (50 ml·min⁻¹ and heating rate of 10 °C·min⁻¹) and after a cleaning treatment (He flow at 150 °C for 2 h). Hydrogen consumption was calculated after a calibration with CuO.

The Raman equipment used (Jobin-Yvon Horiba coupled to an Olympus microscope with a lens of 50x/0.5 LMPlanFI and He/Ne laser excitation source (633 nm), resolution of 3 cm⁻¹) also belongs to the SSTTI at the University of Alicante. Its calibration was carried out by checking the Si signal at 520 cm⁻¹.

The morphology of the samples was studied with micrographies obtained using a JEOL electron microscope (model JEM-2010), working at 200 kV. The device contains an OXFORD INCA Energy

TEM 100 analytical system and a SIS MegaView II camera. Samples before analysis were reduced in the same conditions as XPS experiments, and then, suspended and placed on copper grids.

Catalytic tests with 100 mg of sample were carried out in a reaction system connected to a gas chromatograph (Agilent Technologies, 7890A model). Previously to the reaction, samples were reduced with a hydrogen flow until they reached the reaction temperature (400 °C, ramp 5 °C·min⁻¹), and then the reaction was carried out within 24 h approximately. Reaction conditions were: 15% CO₂ and 15% H₂, balanced with He, with a total gas flow of 50 ml·min⁻¹. CO₂ conversion and CO selectivity were calculated using the following equations:

$$X \text{ CO}_2(\%) = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \cdot 100 \quad \text{Equation 2}$$

$$S \text{ CO}(\%) = \frac{[\text{CO}]_{\text{out}}}{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}} \cdot 100 \quad \text{Equation 3}$$

RESULT AND DISCUSSION

1. Thermogravimetric analysis of materials before pyrolysis

The decomposition temperatures of the MOF and the MOF impregnated with the ceria precursor, were studied under inner atmosphere. Figure 1, shows the thermogravimetric analysis of Cu₃(BTC)₂, denominated as Cu(BTC), and the same material impregnated with two different amounts of ceria precursor, with Cu:Ce atomic ratios of 20:80 (20Cu80Ce) and 40:60 (40Cu60Ce). As we can see, the Cu-BTC material has two well defined weight losses: one below 100 °C, that is when the solvent starts to be desorbed, and another one at a higher temperature (350 °C), that corresponds to the sample decomposition. This decomposition temperature is normally found for this type of materials[30]·[31]. If we calculate the residual amount of solid remaining after the total decomposition, we can see that 67 wt.% is left (we are taking into account the solvent loss below 100 °C, since it does not take part of the MOF). This percentage perfectly fits with the theoretical amount of Cu plus C present in the MOF, the HKUST-1 molecular formula being C₁₈H₆CuO₁₂; it points out that the MOF decomposes into C and metallic Cu. When the MOF is impregnated with the ceria precursor ((NH₄)₂Ce(NO₃)₆) the onset temperature of decomposition of the system is 260°C. It is due to the decomposition of the ceria precursor that generates NO_x, [32] · [33]. We can also see a weight loss around 340 °C, which is ascribed to the decomposition of the MOF itself. Actually, the sample containing less HKUST-1 (20Cu80Ce) presents a less pronounced weight loss at 340 °C. These results show an important factor we need to take into account for proposing a safe and efficient method to prepare our catalysts. The large amount of hazardous gases produced (NO_x) and their fast production guide us to use a high-pressure reactor that can withstand the possible and sudden increase of pressure. Furthermore, we also used these experiments to set the pyrolysis temperature of the catalysts (550 °C). At this temperature, we are sure that the MOF and the ceria precursor have fully decomposed.

Figure 1. Thermogravimetric profiles of the parent Cu-BTC and the impregnated Cu-BTCs with different compositions: 20Cu80Ce and 40Cu80Ce.

2. Catalytic testing of the first generation of catalysts

The properties of the catalysts are obviously affected by the way they are prepared. The first parameter that we checked was the effect of the catalysts composition. For that reason, we prepared a catalyst in which we aimed to have two different Cu contents. In this way, we impregnated the HKUST-1 with two different amounts of ceria precursor targeting two molar ratio 20Cu:80Ce and 40Cu:60Ce. The second studied parameter was the decomposition method. We carried out the decomposition following the two procedures described in the experimental section, labelled as P and Pf. In both cases, we used N₂ atmosphere and a pressure of 1 Bar.

Figure 2 reports the catalytic activity of the above-mentioned samples. As we can see, the samples having high Cu content show poor catalytic activity, with solid P₄₀₋₆₀ (N₂, 1 bar) being completely inactive. The catalyst Pf₄₀₋₆₀ (N₂, 1 bar) has some activity during the first stages of the reaction, but the conversion level is as low as 1% after 20 hours on stream. In spite of the fact that these samples have higher amount of Cu species, the conversion is much lower than that of their counterparts. It is important to remark that the selectivity is 100% towards CO. The catalysts with low Cu content show a better catalytic behavior in the RWGS reaction. Thus, sample Pf₂₀₋₈₀ (N₂, 1 bar) produces an initial conversion of 16 % which decreases up to 9 % after 20 h on stream. The sample prepared by the P method and low Cu content behaves worse than the sample prepared by the Pf method, but still shows catalytic activity. It can be summarized that a high Cu content diminish the catalytic activity, and that the Pf method yields gives better catalysts than the P method.

Figure 2. CO₂ conversion versus time on stream for four different catalysts.

In order to see the influence of the copper loading the results have been plotted as mmol CO₂ converted per minute and per gram of copper (see supporting information fig S5). We can see that the difference in catalytic activity between samples having low and high content of copper is very pronounced, being the one having low Cu content the most active one. However, we have to remark that in this reaction both, copper and ceria, participate in the catalytic cycle and this comparison does not take into account the influence of the ceria support.

3. Characterization of the first generation of catalysts

In order to elucidate the properties of the prepared catalysts and how they affect to the catalytic performance, we have carried out a complete characterization study by using a wide variety of techniques. Figure 3 show the XRD patterns of the prepared catalysts. We can see the characteristic peaks of the cubic fluorite structure of ceria. It is surprising to see how the samples with high ceria content (20Cu80Ce) show less defined peaks, this indicating lower crystallinity. It is counter intuitive, since one might expect larger ceria crystal in samples having higher amount of ceria. This result indicates that the MOF matrix or Cu play an important role in the formation of ceria crystals. It is also important to remark that in the 20Cu80Ce samples no peaks of copper oxide or metallic copper were detected. Taking into account that the total Cu content is 7.7 wt.% in these samples, it should be detectable by XRD. Thus, these results indicate that Cu species are well dispersed all over the support, and their small crystallite size makes them non-detectable by XRD analysis. If we look now up the samples with lower ceria content (40Cu60Ce), we can see the peaks of metallic copper at 43.3° and 51°, copper (I) oxide at 35.8° and 38.9° and copper (II) oxide at 36.7°. It points out that these catalysts contain crystalline copper particles with relatively large crystal size, which is measurable by XRD analysis. This means that catalysts 40Cu60Ce present lower copper dispersion, independently of the pyrolysis method used in their synthesis. Table 2 shows the crystallite sizes of Cu species and CeO₂, calculated using the Scherrer equation. [34] The CeO₂ crystal size for samples

40Cu60Ce is larger than for samples 20Cu80Ce. As it has been mentioned before, the larger the amount of ceria is, the lower the crystal size of ceria becomes. The pyrolysis method does not affect much the crystal size of the CeO_2 ; thus, the sample pyrolyzed by method P gives an average ceria crystal size of 22 nm, while the Pf method gives 23 nm, essentially the same. Both the large size of the copper particles and the large ceria crystal size might explain the poor catalytic activity of the samples 40Cu60Ce. However, the difference in the catalytic performance of samples 20Cu80Ce (Pf and P) cannot be explained only with the XRD results, since copper species are not detected and the crystal size of ceria particles is very similar.

Figure 3. XRD patterns of the different samples. Full circles: CeO_2 fluorite structure; full squares: metallic copper; full triangles: CuO; full stars: Cu_2O .

In order to corroborate these results, we also did Raman spectroscopy studies (Fig S1). We could see that all samples show a peak centered at 467 cm^{-1} , which is typically assigned to CeO_2 vibrations and particularly ascribed to the triply degenerated TO mode[35]. The main differences found are that samples with high Cu loading show two additional peaks at 223 and 292 cm^{-1} , which are ascribed to the vibrational mode of CuO. This means that the high copper loading samples have larger CuO particles, in agreement with XRD.

Table 2. Crystallite size of Cu and CeO_2 calculated using the Scherrer equation.

Catalyst	2θ	D Cu, nm	2θ	D CeO_2 , nm
P ₂₀₋₈₀ (N ₂ , 1bar)		-	28.6	22
P ₄₀₋₆₀ (N ₂ , 1bar)	43.3	27	28.6	35
Pf ₂₀₋₈₀ (N ₂ , 1bar)		-	28.6	23

Pf₄₀₋₆₀ (N₂, 1 bar)

43.3

32

28.6

33

In order to get further insight into the properties of the catalysts, especially in terms of redox properties, we carried out temperature-programmed reduction (TPR) experiments. The analysis of the results provided by these experiments is far from being trivial, since every copper and ceria species can be reduced at different temperature depending on their particle size, oxidation state or interactions among the different species. We analyzed CuO and CeO₂ as reference materials. Figure S2 shows the TPR profile of both materials; where it can be seen that the CuO profile presents a broad peak centered at 320 °C, while the reduction of ceria takes place in two different processes; one at low temperature (450 °C) where the surface ceria is reduced, and another one at high temperature (800 °C) where the bulk ceria is reduced.

Three well defined peaks can be seen in the TPR profiles of our samples (Fig. 4): the peaks so-called α , β , and γ peaks [36],[37], all of them located at lower temperature than the reduction of pure copper or pure ceria. In literature, we can find two types of TPR profile for CuO_x/CeO₂: the two steps reduction [38] and the three steps reduction profiles [39],[26]. In the most complex system when three peaks are found, the assignation of the peaks is as follow. There is a lot of literature explaining these three peaks in a slightly different way. The α peak (at lowest temperature) is due to the reduction of highly dispersed CuO_x species, which are in close contact with the support. The assignation of this peak is very straightforward and there is an agreement between different research groups developing CuO_x/CeO₂ catalysts[8,40–42]. The β peak is ascribed to the reduction of CuO_x particles well dispersed on CeO₂. The assignation of this peak has been studied by Flytzani *et. al.* [42] and others [8],[43], who have ascribed this peak to these type of species. Finally, the γ peak corresponds to the reduction of the larger CuO particles. It is generally assumed that the lower the temperature of reduction, the smaller the particles size and the stronger the CuO_x-CeO₂ interaction[44],[37].

Thus, it is clear that the sample Pf₂₀₋₈₀ (N₂, 1 bar) presents the α , β , γ peaks at lower temperatures than its counterparts, this indicating the small copper oxide particle size. When the pyrolysis is carried out using the P method, the peaks shift at higher temperatures and get broader, this indicating that both the particle size is larger and particle size distribution is wider. The samples having high Cu content (40Cu60Ce) showed a very broad band in which is difficult to distinguish the α , β , γ peaks. It points to a very poor dispersion of the copper particles, as it was also shown by XRD analysis.

Furthermore, we could also quantify how much hydrogen was consumed (Table 3) during the reduction processes. The samples pyrolyzed using the Pf method show more hydrogen consumption than the samples prepared by the P method, independently of the copper content. This fact is surprising, since one can think that the higher the content of copper the more hydrogen would be consumed. However, a high Cu content implies the decomposition of a larger amount of HKUST-1, this producing a more reductor environment. The linker of the MOF can act as a reductor agent and generate metallic copper, which explains the lower hydrogen consumption in TPR experiments: an important amount of copper species are already reduced upon the MOF decomposition. Actually, the diffraction peaks corresponding to metallic copper particles (peaks at 34° and 51°) are clearly evidenced in the XRD patterns. The reduction of the metal oxide during the thermal decomposition of a MOF has been already demonstrated by Santos *et. al.*[45,46]. They used Fe-BTC metal organic framework or MIL-100 to prepare highly active Fischer-Tropsch catalysts. With the use of X-ray absorption measurements together with Mössbauer spectroscopy they demonstrated that during the thermal decomposition of the MOF cationic iron was reduced to metallic Fe. Moreover, iron carbide could be formed if the temperature of decomposition was high enough. In our case, we decomposed also the ceria precursor, thus generating NO_x that has a high oxidant character. In this way, we have a competition between the reductor character of the linker (carbon material) and the oxidant character

of the NO_x . So, if we want to increase the copper content we produce a more reductor environment, since we decompose a larger amount of MOF.

The duration of the pyrolysis treatment also affects significantly the redox properties. Thus, the TPR profile of catalyst P_{40-60} (N_2 , 1 bar) shows a very weak feature of copper oxide reduction. In this case the amount of linker is higher and the time of pyrolysis is longer, so most of the copper oxide is reduced upon the pyrolysis treatment. Metallic copper sinters at lower temperatures than copper oxide [47]. Actually, the reduction assisted sintering of copper particles is widely used in electronics to lower the sintering temperature. As a consequence of getting reduced Cu species, we get large copper particles having poor redox properties and poor catalytic activity [47].

Figure 4. TPR profiles of the different catalysts.

We have checked the oxidation state of copper species after the pyrolysis treatments by X-ray photoelectron spectroscopy and X-ray excited Auger electron spectroscopy (XAES). Fig. 5 shows the $\text{Cu } 2p_{3/2}$ core level of all the catalysts prepared. The profile of the spectra already shows the high heterogeneity of the samples. Binding energies above 933.5 eV and the presence of shake-up peaks are characteristic of CuO species, while binding energies below 932.5 eV are typically assigned to Cu_2O or metallic copper. For all samples, we can see that CuO is present as well as Cu_2O or metallic copper. Samples having low Cu content present more defined peaks at high binding energies, indicating the higher concentration of CuO (as we could already conclude from the TPR profiles). The samples having high Cu content show signals at low binding energies. These results are also in line with the TPR profiles and confirm that the linker decomposition produces a reductor environment and, consequently, higher amount of reduced copper particles with a poor dispersion.

The analysis of $\text{Cu } 2p_{3/2}$ core level is especially difficult. Since the Cu^+ and metallic copper have statistically the same binding energy, they are difficult to distinguish. XAES is more suitable for distinguishing between Cu^+ or Cu^0 . Fig 6. shows the XAES spectra at the LMM Auger transition for the four samples. It can be observed that the sample having low Cu loading presents two clear bands. One centered at 917.5 eV that is ascribed to Cu^0 , and a second one at lower kinetic energy that ascribed to Cu^+ . [26,48–50] It points out that even for low Cu content, some of the copper is reduced. However, for the samples having high Cu content only one peak centered at 917.5 eV is detected. It indicates that the presence of the linker pushes the reduction of Cu^{2+} to Cu^0 , since no Cu^+ was found.

This fact is another evidence that our pyrolysis methods generate a reductor environment that promotes the reduction of copper, while when more linker is present in the pyrolysis the more reductor environment is achieved.

Before reaction, the catalysts are activated at 400 °C under flowing hydrogen in order to reduce the CuO species and enhance the Cu-CeO₂ interaction. For that reason, we have also analyzed the XPS spectra of the samples after reduction. Fig. 5 shows the Cu 2p_{3/2} transition of this catalysts and we can see that the signal can be deconvoluted into two peaks. The more intense one at low binding energy [48] is ascribed to metallic copper species. It was also corroborated by XAES looking at LMM transition. The second peak at higher binding energy must be associated to Cu²⁺. However, its intensity is very low and the satellite peaks associated to Cu²⁺ are hardly detected [7,26,28,51].

We can say that after reduction at 400 °C the copper species are reduced to a large extent in all the catalysts. The main difference between catalysts with high and low copper loading is the position of the Cu 2p_{3/2} peak. For samples 20Cu40Ce, it is located at lower binding energies. This can be attributed to an electron enrichment of the Cu species produced by their strong interaction with ceria, as we have previously demonstrated for different metals supported either on ceria or on other reducible supports[28,52,53]. The better dispersion of the CuO particles in the 20Cu40Ce catalysts leads to a better interaction of the reduced copper species with the ceria support. This strong interaction seems to be crucial for the catalytic performance, since samples having high loading of Cu show very poor catalytic activity or do not have activity at all. It is interesting to mention that in all samples a peak appears at higher binding energies (around 933.5 eV), indicating that copper is not fully reduced to the metallic state.

Figure 5. Cu $2p_{3/2}$ core level spectra of the different catalysts. A) unreduced catalysts, B) reduced catalysts (400 °C flowing hydrogen 1h).

Fig. 7 shows the transmission electron microscopy images of the samples. As we can see, the morphology of the samples with high Cu loading is totally different to that of their counterparts with lower Cu content. We can see that samples 20Cu80Ce present a very homogeneous aspect. There are dark spots homogeneously distributed and we could not see agglomerates. It is difficult to observe differences between samples P₂₀₋₈₀ (N₂, 1 bar) and Pf₂₀₋₈₀ (N₂, 1 bar). Thus, it should be emphasized that, despite having high ceria content, the particles are very finely dispersed.

Samples 40Cu60Ce show large crystals with different contrast that can be interpreted as due to the presence of both CuO and CeO₂ crystals. This is consistent with the finding obtained with other characterization techniques.

Bearing in mind all the results presented above, we observe that the crystal size of ceria and copper oxide is critical for the catalyst performance. Some of the results are in line with traditional synthetic routes: high copper loading leads to low copper dispersion. However, it is interesting to notice that the ceria crystal size is smaller in catalysts with the largest ceria content, what is related to the MOF matrix and to the way the catalysts are prepared.

Figure 6. XAES at the LMM transition for the four samples studied.

4. Synthesis, characterization and catalytic testing of the second generation of catalysts

We have also learnt that the reductive environment generated during the pyrolysis of the catalysts' precursor leads to the reduction of CuO to copper, thus favoring the sintering of the particles. In order to avoid this reduction, it might be interesting to pyrolyse the samples in an oxidant environment. To do so, we used air instead of nitrogen during the pyrolysis and we continued studying the samples with low Cu content in such a way that the amount of linker present is diminished.

Figure 6. TEM images of the different samples.

Figure 8 reports the catalytic activity of sample Pf₂₀₋₈₀ (Air, 1 bar). For the sake of clarity, we have also included in the figure the catalytic behavior of sample Pf₂₀₋₈₀ (N₂, 1 bar). As one can see, the

sample obtained by pyrolyzing the precursor in air has higher catalytic activity (CO_2 conversion) compared to the sample pyrolyzed in N_2 . If we assume that during the air pyrolysis we burn off all the carbon residue, the content of Cu increases from 7.7 wt.% for sample Pf_{20-80} (N_2 , 1 bar) to 8.4 wt.% for sample Pf_{20-80} (Air, 1 bar). However, the conversion increases $\sim 7\%$. This increase in conversion cannot be explained only by the increase in Cu loading but by the different physico-chemical properties of the final catalyst such as Cu dispersion and electronic properties, which can also be modulated by the different copper-ceria interaction.

Figure 7. Comparison of the catalytic performance of the samples Pf_{20-80} (Air, 1bar) and Pf_{20-80} (N_2 , 1bar) in RGWS.

We have also analyzed the sample prepared in air by XRD, TPR, TEM and XPS. In order to not enlarging excessively this paper, we only include in the paper the TEM and the XPS results. The results of the other techniques are included as Supporting Information. Summarizing them, XRD analysis shows only the cubic structure of the ceria support (having an average crystal size of 22 nm) and copper species were not detected. The TPR profile of the sample Pf_{20-80} (Air, 1bar) shows three well defined peaks α , β , γ , which are located at the same temperature than for the sample Pf_{20-80} (N_2 , 1bar), pointing out a good dispersion of the CuO particles.

The TEM images (Fig. 8) show that the Pf_{20-80} (Air, 1bar) catalyst is homogeneously distributed in dark tiny spots. We have not analyzed the sample statistically due to the difficulty for distinguishing between CuO and CeO_2 crystals (very similar contrast), but the general view of the sample indicates that the crystals present in the sample are very well spread, giving us the first evidence that CuO is well dispersed.

Pf_{20-80} (Air, 1bar)

Figure 8. TEM images of sample Pf₂₀₋₈₀ (Air, 1bar)

XPS can give us evidences of the electronic nature of copper before and after the catalyst is reduced. Fig. 9 shows the Cu $2p_{3/2}$ core level spectra of Pf₂₀₋₈₀(Air, 1bar) catalyst (for the sake of comparison, the Cu $2p_{3/2}$ spectra of the sample Pf₂₀₋₈₀(N₂, 1bar) was plotted in the same graph). The spectra of the sample Pf₂₀₋₈₀(Air, 1bar) presents the characteristic peaks of oxidic copper. The peak ascribed to the reduced copper (below 932 eV) is not detected, while it could be observed in the spectra of the sample pyrolyzed under N₂ atmosphere. It points out that during the decomposition in the presence of air, the production of less reduced copper is favored.[7]

When we reduced the samples at 400 °C under flowing hydrogen, copper species are fully reduced in catalyst Pf₂₀₋₈₀(Air, 1bar) (Fig. 9), while for catalyst Pf₂₀₋₈₀(N₂, 1bar) there are still some residual oxidized species. It indicates that the copper species present in catalyst Pf₂₀₋₈₀(Air, 1bar) are smaller and strongly interacting with the CeO₂ support. Consequently, they can be reduced easier than the Cu species of Pf₂₀₋₈₀(N₂, 1bar), since the interaction is enhanced and the redox synergy (Cu-Ce) favors the reducibility[44]. Furthermore, the peak in the $2p_{3/2}$ spectra of sample Pf₂₀₋₈₀(Air, 1bar) is located at a lower binding energy (around 0.3 eV less) than that of catalyst Pf₂₀₋₈₀(N₂, 1bar). It indicates that the copper in the former are electron-enriched, what seems to be crucial for the catalytic performance.

Figure 9. Cu $2p_{3/2}$ core level spectra of the different catalysts, Pf₂₀₋₈₀ (Air, 1bar) and Pf₂₀₋₈₀ (N₂, 1bar). A) un-reduced catalysts, B) reduced catalysts at 400 °C under flowing hydrogen atmosphere.

We have also calculated the surface composition of these two samples from the XPS data. Table 3 shows the surface Cu/Ce atomic ratio found in the catalysts before and after reduction. The percentage of Ce(III) found in the samples, as obtained from XPS analysis, has also been included. Firstly, the amount of Ce(III) increases a similar extent, with the reduction process. But, what is more important, the final surface Cu/Ce ratio, as obtained by XPS, is clearly affected by the atmosphere at which the catalysts precursor has been pyrolyzed, and by the reduction treatment. Thus, the sample obtained by pyrolysis under nitrogen (Pf₂₀₋₈₀ (N₂, 1bar)) contains a lower relative amount of surface copper than the catalyst obtained by pyrolysis under air (Cu/Ce 0.16 vs. 0.28). But the behavior during the reduction treatment is opposite, as it produces a strong surface segregation of copper in the former, and an important decrease of the surface Cu content in the catalyst obtained under oxidative pyrolysis. As reported by other authors, [34,37] this surface migration of ceria is indicative of a strong metal-support interaction effect. It is clear for the catalytic results we have obtained with these catalysts that the induction of this strong copper-ceria interaction is crucial in the reverse water-gas shift reaction.

Table 3. Atomic percentage of Ce(III) and atomic ratio Cu/Ce calculated by XPS.

	Ce (III) (%)	Cu/Ce
Pf ₂₀₋₈₀ (N ₂ ,1bar)	31.20	0.16
Pf ₂₀₋₈₀ (N ₂ ,1bar) Reduced	34.50	0.48
Pf ₂₀₋₈₀ (Air,1bar)	32.63	0.28
Pf ₂₀₋₈₀ (Air,1bar) Reduced	34.34	0.14

In order to compare our preparation method with a conventional one, we have prepared a reference catalyst containing 8 wt.% Cu loading supported on ceria. For the preparation of this catalyst we have used an optimized impregnation method to get high copper dispersion and interaction of the metal with the support (see experimental section). The physicochemical properties of this catalyst are reported elsewhere[26]. Figure 10 shows the comparison of the best catalyst prepared in this work with a reference catalyst prepared by traditional impregnation method. As we can see, the reference catalyst has an initial activity higher than the one prepared from the Cu MOF. However, for the reference catalyst the deactivation is more pronounced and after 20 h it shows lower conversion than our catalyst. It indicates that our catalyst deactivates in a lesser extent than when is prepared using a traditional method.

CONCLUSION

We have found that the pyrolysis conditions of the impregnated MOF are critical to get active and selective catalysts in RWGS. By changing the pyrolysis atmosphere we can get an oxidant environment that keeps copper oxidized during the decomposition and prevents sintering. We can summarize that the presence of air in the decomposition induces the formation of copper oxide species, which have more difficulties to sinter than metallic copper. It favors the interaction with the ceria support and consequently it leads to a better catalytic performance. In this way, we can prepare highly CuO dispersed on CeO₂ that can be easily reduced and interact strongly with the ceria. All these factors make this catalyst the most active among the ones prepared here. Furthermore, the

catalysts we prepared here outperform the same catalysts prepared by a traditional method such as wet impregnation using conventional metal precursors.

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