

Review

Copper–Zirconia Catalysts: Powerful Multifunctional Catalytic Tools to Approach Sustainable Processes

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Abstract: Copper–zirconia catalysts find many applications in different reactions owing to their unique surface properties and relatively easy manufacture. The so-called methanol economy, which includes the CO₂ and CO valorization and the hydrogen production, and the emerging (bio)alcohol upgrading via dehydrogenative coupling reaction, are two critical fields for a truly sustainable development in which copper–zirconia has a relevant role. In this review, we provide a systematic view on the factors most impacting the catalytic activity and try to clarify some of the discrepancies that can be found in the literature. We will show that contrarily to the large number of studies focusing on the zirconia crystallographic phase, in the last years, it has turned out that the degree of surface hydroxylation and the copper–zirconia interphase are in fact the two mostly determining factors to be controlled to achieve high catalytic performances.

Keywords: zirconia; copper; interphase; acid–base properties; DHC; methanol economy

1. Introduction

Zirconia-based oxides are receiving increasing attention from the scientific community as heterogeneous catalysts and supports for metal nanoparticles, owing to their tunable phase composition, redox, and acid/base properties. The combination between zirconia and copper is a fruitful union that leads to multifunctional catalysts showing high activity and selectivity in different classes of reaction and, in particular, in processes linked to methanol economy and (bio)alcohols upgrading. Such a wide range of applicability is due to the fact that these materials have relevant acid/base and redox properties, and they can also give spill-over and other interphase phenomena, coupled with the typical activity of the metal-supported catalysts [1–8]. Furthermore they have some advantages in terms of activity, stability, toxicity, and cost compared to materials based on precious metals, ZnO, and/or mixed oxides. Despite being studied since from the beginning of the 1990s, the full potential of copper–zirconia catalysts has still to be exploited, while the reasons for their activity is still a matter of debate and some inconsistencies can be found in the literature, especially related with the zirconia polymorphs' features and activity. In this review, the properties and the main applications of copper–zirconia catalysts are critically analyzed, and the most impacting parameters on the catalytic activity are discussed.

2. Preparation and Properties of Copper–Zirconia Catalysts

Several parameters must be taken into consideration when preparing a copper–zirconia material. An attempt to sum up the main factors influencing the activity of the final material is provided in Figure 1.

Zirconia is employed in three different polymorphs (monoclinic, tetragonal, and cubic—m-ZrO₂, t-ZrO₂ and c-ZrO₂), and also in an amorphous phase (a-ZrO₂). The phase composition affects the acid–base and textural properties of the resulting material, and it can be tailored by thermal treatments

and by the presence of other elements (e.g., Si, Y, La). The structure–activity relationships of zirconia phases are controversial and not clearly understood, which is further complicated by the wide number of preparation techniques.

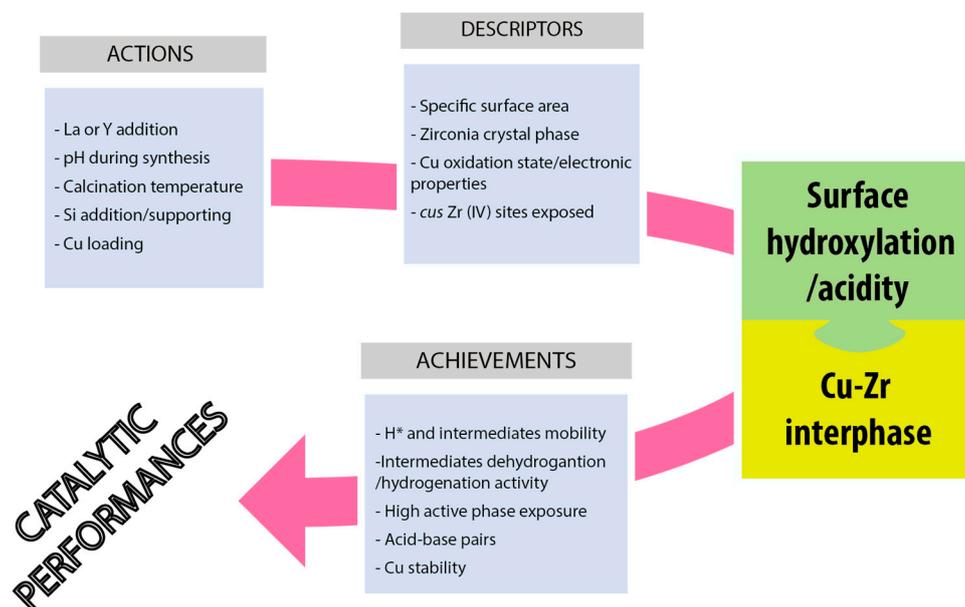


Figure 1. General guidelines for the preparation of an active copper–zirconia catalyst.

Tetragonal ZrO_2 is the most frequently used, and it is often considered as the best choice in terms of acid properties and oxygen vacancies compared to the monoclinic ZrO_2 , but the results are not univocal [1,2,9–14]. On the other hand, amorphous zirconia, in spite of a non-crystalline nature, has a higher surface area, thus leading in several cases to a catalyst showing superior performances, as shown especially in some recent works [2,4,5,15,16].

The properties of the zirconia polymorphs have been suggested to impact the copper dispersion and its oxidation state. It is reported that oxygen vacancies stabilize both Cu^+ cations and thermodynamically unstable tetragonal phase [2,9,17], but some authors suggest that this kind of defect can be easily found also on monoclinic zirconia [18,19]. At the same time, it is reported that higher copper dispersion is reached over tetragonal zirconia, with some exceptions, especially in the case of high surface area amorphous ZrO_2 [2,4,17–19].

The stabilization of Cu^+ is often invoked as crucial for the activity in some reactions [2,9,20] being an acid site. However, some of us have recently described that even very small metallic copper and CuO nanoparticles can express an unusual acidity [4,5,21,22], therefore moving on from the presence of Cu^+ .

The doping of zirconia is a strategy to improve several features. Ions with a valence lower than +4 (e.g., Y and La) favor the formation of oxygen defects [2,23–27], while Si is used to avoid the crystallization of ZrO_2 at high temperatures to preserve the high surface area of the amorphous structure [4,5,28]. It is worth noting that most of the synthetic procedures reported in the literature involve the use of basic solutions, and involuntary silica contaminations might occur if carried out in classical lab glassware. Even a minimum amount of Si is enough to drastically change the phase composition of the resulting Zr material. This may further complicate the rationalization of the results reported in the literature.

In conclusion, zirconia phase composition clearly has a dramatic effect on the catalytic behavior of the final material; however, actually, the effect cannot be rationalized or clearly explained. Despite the large number of studies on this topic, the only trend observed so far with a good approximation is that the better the Cu dispersion, the higher the activity of the catalyst.

When preparing a copper–zirconia catalyst, two main general strategies may be adopted. The first one consists of the addition of the Cu during the step of zirconia preparation (e.g., co-precipitation and sol–gel methods). Typically, precursors of copper, such as copper nitrate, and zirconium, such as zirconyl chloride or nitrate, are combined to form the starting mixture; then, the procedures reported in the literature differ for temperature, pH, aging time, precipitating agent, and/or additional metal/co-oxide precursors. In the second approach, copper is added after ZrO_2 has been synthesized (e.g., impregnation techniques, chemisorption–hydrolysis). Sputtering [29] and grafting [30] methods have been also used with the aim of clarifying reaction mechanisms and active sites. The preparation method impacts the properties of the resulting materials, such as the dispersion of copper and on its phase composition.

In principle, co-precipitation techniques may be advantageous in terms of copper dispersion; however, some incorporation of Cu species into ZrO_2 lattice occurs. On the one hand, this favors the formation of Cu^+ species, but it also results in a loss of active copper. Depending on the application, this effect is desirable or not [2,4,31,32].

Impregnation methods are simpler techniques that allow one to deposit copper on the surface of zirconia, limiting its incorporation into the lattice [2]. The control of the dimension of the particles and the nature of the copper phase can be achieved by tuning the properties of the preformed zirconia. With respect to the traditional impregnations, a better control on the copper phase might be achieved using some advanced methods [33], such as chemisorption–hydrolysis [5], metal vapor synthesis (MVS), chemical vapor deposition (CVD), or colloidal synthesis, but these protocols are poorly or not studied at all for the preparation of copper–zirconia catalysts.

The calcination is also a very critical step, because copper migrates and agglomerates thus compromising the catalytic performances [34] (Figure 2). This is particularly true for co-precipitation methods, in which the thermal treatment causes also the zirconia phase transformation.

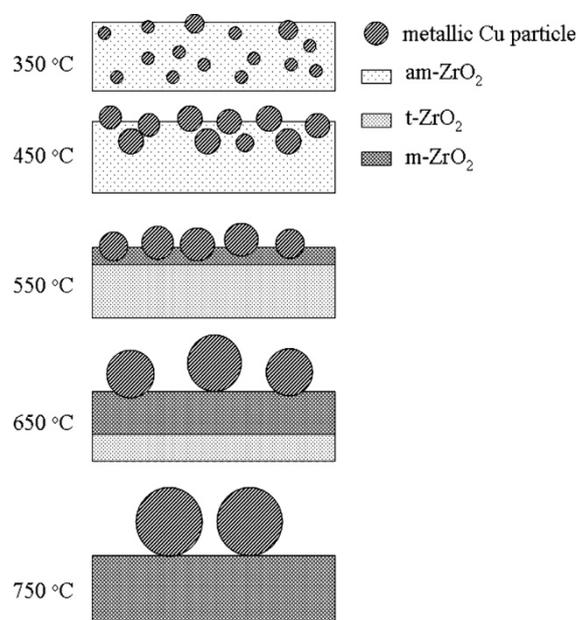


Figure 2. Schematic representation of the influence of the calcination temperature on the phase composition and copper particles size on a copper–zirconia material (<https://pubs.acs.org/doi/10.1021/jp075930k>) [34]. Reprinted with the permission of the American Chemical Society (ACS); further permissions related to the material excerpted should be directed to the ACS.

A parameter that helps obtain a very finely dispersed copper phase is obviously the maximization of the surface area of the material. As previously mentioned, the use of amorphous zirconia is quite recent [2,4,5,15,16] that allows, for example, synthesizing a catalyst with around 60% of dispersion and

a final surface area of 216 m²/g (before copper deposition, it was 309 m²/g) [4]. Promoters, such as ceria in Cu-Ce-Zr mixed systems, are also commonly used to maximize the copper dispersion for different applications [35–38].

Alongside the dispersion, a growing number of papers focus the attention on the Cu-Zr interphase as the key aspect for obtaining highly active and selective copper catalysts with improved stability. Clearly, the interfacial area is linked with the dispersion of the copper phase [3,5,29,34,39–43].

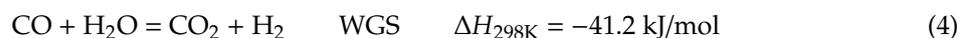
The oxidation state of copper is a parameter that has to be controlled during the preparation of the catalyst or later, by performing a suitable pretreatment (e.g., reduction with H₂) before the reaction. Depending on the application, one may need to stabilize Cu²⁺, Cu⁺, metallic copper, or mixed phases, even though that is not an easy task, in particular in the reaction medium. There is always a large debate on which is the oxidation state active in the reaction, alongside the fact that copper oxidation/reduction processes may occur easily during the reaction, making the understanding of the phenomena even more difficult [4,5,9,14,19,27,44].

3. Copper–Zirconia Catalysts for the Methanol Economy

One of the most widespread uses of copper–zirconia catalysts is in the so-called sustainable methanol economy that includes several processes [6]. The reason is that metallic Cu has a density of the states with the top 3D band completely below the Fermi level, which makes it particularly suitable to interact with methanol ([45] and ref. therein). Other metals, such as Pd [46,47] or alloys [48], are as well active in methanol reactions, but their high cost makes Cu the undisputed leader in this field.

Methanol synthesis (MS) (Equation (1)), also known as CO₂ (or CO) hydrogenation [49–52] and the hydrogen production via methanol steam reforming (MSR) (Equation (2)) [46,53–55], are among the most relevant reactions as they are directly involved in the framework of the CO₂ valorization and the on-board hydrogen generation for transportation applications, respectively [6]. Methanol decomposition (MD) (Equation (3)) [56,57] is another reaction for the hydrogen generation, but it is sometimes is considered competitive of MSR and responsible for the poor CO₂ selectivity.

The water gas shift reaction (WGS) (Equation (4)) and its reverse, namely the reverse water gas shift (RWGS), play a crucial role in controlling the CO selectivity in MS and MSR processes [55,58–60].



Since MS and MSR are in principle the opposite of each other, and MD is often a side reaction in both processes, it is no surprise that a catalyst is active in all these reactions. Naturally, the same applies for copper–zirconia catalysts, and therefore, the output of a process will essentially depend on the feed and the reaction conditions. We will see though that the surface chemistry involved is quite different [54,59,61,62], and many aspects of the catalysts can be tailored to maximize (or minimize) one or the other reaction.

Thus far, many strategies have been used to increase the activity of copper–zirconia catalysts in methanol applications, and much of the research efforts have been directed to identifying the active catalytic site(s) [41,56]. Unfortunately, little attention has been paid in trying to increase the stability of these systems that typically deactivate within a few hours due to Cu sintering [63–65].

Cu catalysts containing zirconia are generally more stable and produce less CO compared to Zn-based ones in MSR reactions [53] and, as illustrated in a recent review by Din et al. [50], higher CO₂ conversions can be obtained in the MS reaction because CO₂ is more easily activated by the acid–base pairs of zirconia support. The reasons are many. First, the zirconia is highly reducible with the easy formation of Zr³⁺ species that allow for the hydrogen spillover [66], which is essential in MS [67],

and these are able to bind the reaction intermediates, as pointed out by Kattel et al. [60] in a work that combines DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) and theoretical investigations. Second, compared to other systems such as Cu/SiO₂ [4], zirconia promotes the Cu reducibility in general, and specifically, Cu on t-ZrO₂ reduces at lower temperature than on m-ZrO₂. A good reducibility is critical to suppress the surface oxidation, as metallic Cu is the active center for the molecular hydrogen activation, in MS, or formation, in MSR and MD. Third, Cu⁺ species, whose role in the reactions has been the specific object of several studies [14,68,69], are not stable under reducing environment but can be stabilized by introduction into the zirconia lattice as they compensate for the negative charge of oxygen vacancies [70].

There has been quite a debate in the literature about which of these factors is the most impacting and how one influences the other. The fact that Cu dispersion should be as high as possible ([53] and ref. therein) is generally accepted, although there is no linear correlation with the activity [71]. Besides the obvious fact that the more Cu exposed, the higher the activity, Mayr et al. [29,42] have shown that is the interface between Cu and zirconia is what actually determines the “movement” of hydrogen species and, in the case of MSR, promotes the CO₂ selectivity.

From the vast work by Bell and co-workers [18,61,62,67,72] at the end of the 1990s, to the more recent investigations by Yang et al. [69] and Larmier et al. [41], just to cite but a few, great advancements have been made in understanding the complete picture of the surface chemistry during reactions with methanol. The main difference between methanol formation (MS) and hydrogen production reactions (MSR and MD) lays in the reactants, meaning that the first step of the catalytic process consists of the adsorption of CO₂ (or CO) and H₂ in the former, and of methanol and water in the latter. The direct synthesis from CO₂ of dimethyl ether (DME) is another reaction of particular interest, as DME can be a hydrogen vector for the on-board hydrogen generation via reforming [73]. Simple Cu/ZrO₂ catalysts do not have the necessary acidity to perform the dehydration of methanol though, and so more acidic materials are typically added, such as zeolites [74] or ferrierite [75]. The reader is referred to the dedicated literature for more insights on this reaction, as it will not be addressed in this review.

During MS, hydrogen is activated by the metallic Cu, and indeed, the CO₂ hydrogenation activity can be promoted by the addition of a second metal, such as Ag [76,77], which facilitates the Cu reducibility and metallic character. CO₂ adsorbs on the zirconia and then is readily transformed into carbonates [62], while with CO, hydroxylated Zr sites adjacent to coordinatively unsaturated (*cus*) Zr⁴⁺ sites contribute to the adsorption, thus producing adsorbed formates (HCOO-Zr) [18]. There is a strong dependence between the polymorph of zirconia, the strength of adsorption, and the acid–base surface properties [9] (Figure 3). The m-ZrO₂ phase has been reported to adsorb more CO₂ than the t-ZrO₂ because of the higher concentration of basic O²⁻ sites and *cus* Zr⁴⁺ Lewis acid sites. Hence, one might think that m-ZrO₂ is the most active in MS, just as reported by Bell and co-workers [18]. However, Samson et al. [9] have recently clarified why the highest methanol formation rates from CO₂ are obtained with t-ZrO₂. This discrepancy can be ascribed to the different preparation procedures of the catalysts rather than to the specific crystallographic phase. A low-pH approach has been preferred by Bell and co-workers [18,61,62,67,72], whereas others have used precipitations [14,64,72,78,79] at basic pH. According to Samson et al. [9], such opposite preparation conditions result in significant differences in the surface hydroxylations and/or Lewis character of the final materials. They have also identified peculiar Cu species nearby oxygen vacancies, which are far more abundant on the (111) facet of the t-ZrO₂, and these are partly reduced to Cu⁺ and act as electron acceptors—that is, Lewis acid centers.

On an industrial scale, methanol is produced from a CO/CO₂/H₂ mixture [6], which is possible thanks to the activity of Cu in the WGS reaction that facilitates the conversion of CO into CO₂. Interestingly, Grabow et al. [80] have shown via a series of theoretical calculations that the presence of CO in the mixture is in fact beneficial as it promotes the removal of OH* species by RWGS reaction from the hydroxylated surface of the zirconia support.

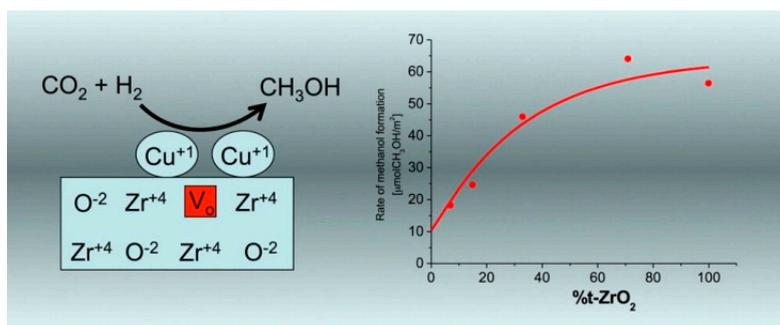


Figure 3. Effect of the percentage of $t\text{-ZrO}_2$ on the methanol synthesis rate [9] (<https://pubs.acs.org/doi/abs/10.1021/cs500979c>). Reprinted with the permission of the American Chemical Society, further permissions related to the material excerpted should be directed to the ACS.

The key factor to be maximized for an active MS catalyst is the Cu–zirconia interaction. Despite the higher concentration of oxygen vacancies in $t\text{-ZrO}_2$, Tada et al. [2,81] reported as more selective to methanol a catalyst prepared on $a\text{-ZrO}_2$. They have used the incipient wetness preparation technique to avoid excessive Cu loss within the zirconia lattice by forming copper–zirconium mixed oxides ($\text{Cu}_x\text{Zr}_y\text{O}_z$). This, along with the weaker adsorption of methanol on $a\text{-ZrO}_2$ that suppresses the MD reaction, results in an active Cu/ZrO_2 with higher selectivity to methanol than those prepared on other polymorphs. Interestingly, the same authors have further developed the catalytic system by studying zirconia–silica mixed oxides [30,82]. They noticed that at the same Cu loading and similar morphological properties of the support, the presence of silica is highly beneficial to the catalytic activity and in particular to the methanol selectivity. This is somehow unexpected, as silica is a rather inert support in MS reaction. By means of an organometallic approach, the authors have prepared a series of silica supports on which isolated zirconium sites are grafted. Then, copper has been added again by grafting technique on the surface hydroxyl groups of the previously anchored zirconium sites. Upon reduction in hydrogen at 500 °C, the so-obtained catalytic system consists of small copper nanoparticles (2.6 nm) with neighboring *cus* zirconium sites (Figure 4). Since the defects invoked for Cu/ZrO_2 catalysts [9] cannot form on such a system, i.e., oxygen vacancies, the source of the enhanced selectivity must be the Zr (IV) sites, as they assist the CO_2 activation and hydrogenation of the intermediates. These findings imply that the amount of zirconia in the supports is not relevant, but rather it is the *cus* Zr (IV) sites exposed that act as Lewis acid centers.

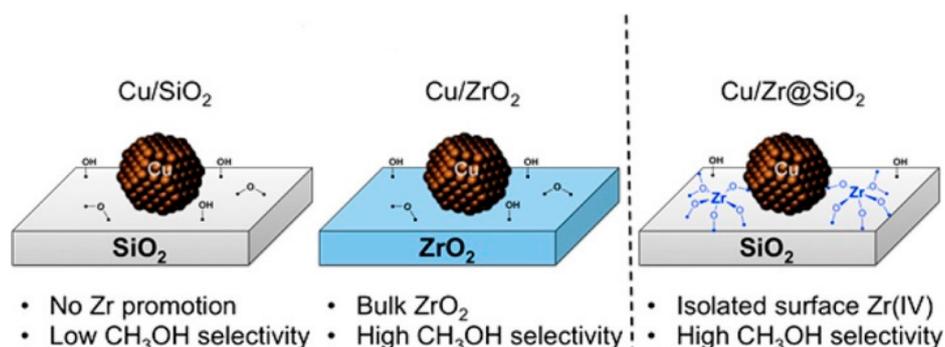


Figure 4. Experimental approach adopted by Tada and co-workers to understand the role of ZrO_2 in CO_2 hydrogenation [30] (<https://pubs.acs.org/doi/10.1021/jacs.8b05595>). Reprinted with the permission of the American Chemical Society, further permissions related to the material excerpted should be directed to the ACS.

A series of theoretical works have shed some light on the actual role of such interphases during the MS reaction. DFT calculations combined with XPS analyses had already revealed that ZrO_2 works as a sort of buffer to accept or release electrons from or to the Cu, which is partly oxidized [83,84].

On this so positively charged Cu, which just for the sake of clarity must be in the form of very small nanoparticles or even clusters, the barrier of H₂O dissociation is small, and the WGS reaction is enhanced [84]. Recently, Polierer et al. [85] have found that the interphase, although critical, is not the adsorption site of the reactants and intermediates during the CO₂ hydrogenation. They have reported a volcano-shaped relation between the activity and the adsorption energy of various sites of a modelled Cu/ZrO₂ system (Figure 5). It is evident how Cu in close proximity to the interphase has the optimal adsorption energy—and in turn highest activity—whereas the interphase and other facets of Cu bind them too strongly or weakly, respectively.

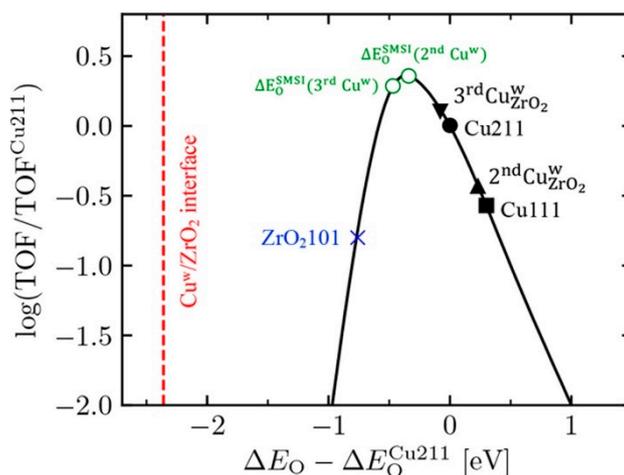


Figure 5. Theoretical activity volcano plot for the hydrogenation of CO₂ to methanol [85]. (<https://pubs.acs.org/doi/10.1021/acs.jpcc.9b06500>). Reprinted with the permission of the American Chemical Society, further permissions related to the material excerpted should be directed to the ACS.

However, there is still debate on which is the precise role of each site and on which reaction pathway is the most favorable [52,60,85–87]. Formate (HCOO) has been recognized in many studies as an intermediate during MS [88] and MSR alike (see below). The following hydrogenation to methanol is carried out by H and OH species spilling over toward the Cu phase. However, Kattel et al. [60] have calculated that over time, the formate species would poison the active sites and thus have proposed a reaction mechanism involving the RWGS reaction followed by CO hydrogenation through the formation of methoxy (H₃CO) species as more likely.

Whichever the reaction pathway, these theoretical studies complete the overall picture at an atomic level of the Cu/ZrO₂ system for MSR reaction, whereby the interphase basically acts as a “bridge” between different catalytic sites. Therefore, a fine control over the Cu nanoparticles size and their interaction with the ZrO₂ phase is key to achieving high catalytic performances [89].

The surface reactivity of MSR is a little different in the sense that the main reactions involved, besides the adsorption of the reactants, are the dehydrogenation and the molecular hydrogen formation. Again, metallic Cu is responsible for the latter [2,62], and without it, MD reactions would occur [61]. The dehydrogenation of the reaction intermediates is more complicated. From the works by Bell and co-workers [18,61,62,67,72], it is known that methanol and water adsorb on the surface of zirconia as methoxy and -OH groups, respectively. Then, as reviewed by Yong et al. [54] and shown via DFT calculation by Lin et al. [90], they must travel all the way to the Cu, and in particular to Cu⁺ sites, where they are dehydrogenated to formates and to CO₂. Indeed, the CO₂ formation is the most delicate of the steps [29,79,91], whereby most of the Cu-based catalysts ([53] and ref. therein, [71,92]), including the commercial one [93], typically suffer from fairly high CO selectivity.

A straightforward strategy to promote the CO₂ formation consists in working at low temperatures (180–220 °C) where the WGS reaction favors the conversion of CO to CO₂. There are already some publications in this direction [93,94]. For instance, Azenha et al. [94] have described a quite active

CuPd catalyst on m-ZrO₂ active at 180 °C (Figure 6). Alternatively, CeO₂ is introduced into the zirconia support, due to its widely known oxygen storage capabilities, with good results in terms of CO suppression, such as those reported by Baneshi et al. [95] and Das et al. [96].

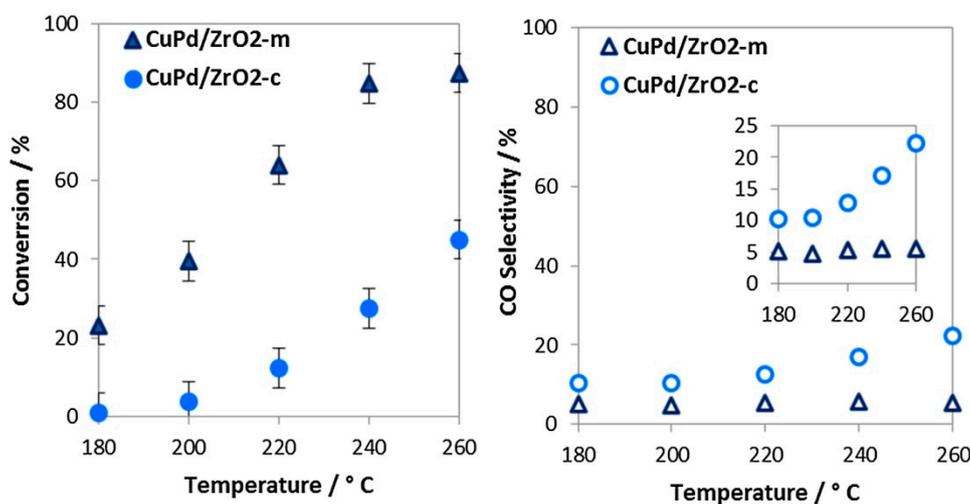


Figure 6. Cu-Pd catalysts on c-ZrO₂ and m-ZrO₂ for low-temperature steam reforming of methanol [94]. Reprinted with the permission of Elsevier.

However, as pointed out by Mayr et al. [29,42], the factor most affecting the CO₂ selectivity is the Cu-ZrO₂ interface. Therefore, Cu nanoparticles as small as possible are highly desirable, and indeed, the addition of zirconia to a Cu/ZnO catalyst has been reported by Matsumura et al. [64] to decrease the Cu particle size with an increase in catalytic activity.

Smaller Cu nanoparticles with strong interaction with the support are useful to increase the stability of the catalysts during the reaction [63], and the preparation procedure can have a significant impact on the final Cu dispersion. For instance, Zhou et al. [14] have shown that by using a fractionated precipitation method to prepare a Cu/ZrO₂ catalyst, the Cu dispersion can be increased—although remaining low compared to other systems [4,97]—with a significant gain in stability.

Similar to the case of MS discussed above, the use of crystalline zirconia is limiting and a-ZrO₂ with its higher surface area might be a better support in this sense. Lytkina et al. [98] and Wang et al. [34] have illustrated how the calcination temperature can impact on the zirconia support and in turn on the catalytic activity, indicating the 350 °C temperature as the maximum to avoid the zirconia crystallization and Cu sintering. Likewise, Yao et al. [71] have obtained a catalyst on a-ZrO₂ with high Cu dispersion and high activity stable up to 50 hours by using an oxalate gel co-precipitation method.

The presence of Cu⁺ sites has been for long considered necessary to the MSR reaction [14,78,96,99,100], and Yang et al. [69] have clarified their decisive role in the dehydrogenation of the methoxy intermediates. Similar to the MS reaction, these sites basically act as Lewis centers [9]. However, there is an intrinsic limitation with the presence of both metallic Cu and Cu⁺, which is a splitting of the roles that results in an “effective” Cu participating to the overall reaction lower than the theoretical. Moreover, the fact that the adsorption sites and the reaction sites might be distant forces the adsorbed intermediates to travel onto the surface of the catalyst, thus slowing down the reaction and/or leading to side-reactions such as MD. Some of us [4] have developed a Cu/ZrO₂ catalyst modified with silica featuring electron-poor Cu nanoparticles that act both as adsorption centers for the methanol and as dehydrogenation sites with the zirconia contributing to the supply of -OH groups from the water activation. In this way, we obtained a 3.5 times higher hydrogen productivity compared to the parent Cu/ZrO₂ catalyst.

In conclusion of this section on the use of copper–zirconia catalysts in the methanol economy, it emerges that the comprehension of the reaction mechanisms, and how they are impacted by these

catalysts, has made relevant steps forward. The efforts devoted to elucidating which of the crystal phases of the zirconia is more active in a specific reaction arrived at the conclusion that the surface acid–base properties, and to a lesser extent the oxygen vacancies, are by far more important factors. Metallic Cu is the active phase that is responsible for the molecular hydrogen formation (or activation), with the hydrogen species being transferred from (or to) the intermediates via the Cu⁺ sites. The use of α -ZrO₂ with its high surface area, and its good interaction with Cu that maximizes the dispersion, looks the most promising catalytic system for methanol applications.

Further research is needed to elucidate the role of the specific acid–base species on the activity and how to optimize their population. For instance, Samson et al. [9] have shown how the MS activity is bound to the acidity, but the precise role of the Lewis and Brønsted species remains elusive. Since the acidity is so critical, tuning the electronic properties of the Cu nanoparticles might be an interesting tool to preferentially direct the reactions to more convenient pathways. Finally, more efforts must be devoted to the stabilization of the Cu phase. Small Cu nanoparticles have displayed longer activity than bigger ones, but they are still unfit for real applications. Dispersing the Cu–zirconia phase on other supports, such as silica [97], might be an option. In Table 1, we summarize the catalytic behavior for the copper–zirconia catalysts reported in this review in MS and MSR.

Table 1. Comparison between the catalytic behavior for the copper–zirconia catalysts reported in this review in methanol synthesis (MS) and methanol steam reforming (MSR) reactions.

Catalyst	Reaction	Preparation Procedure	Reaction Conditions	Catalytic Performances	Ref.
Cu/ZrO ₂ (80 wt % Cu)	MSR	Co-precipitation	S/C = 1.5; T = 250 °C	Prod. H ₂ = 400 mmol g _{cat} ⁻¹ h ⁻¹ Conv. = -; Sel. CO < 0.1%	[78]
Cu/(t- and m-)ZrO ₂ (13 wt % Cu)	MSR	Microemulsion technique	S/C = 1.0; T = 250 °C	Prod. H ₂ = -; Conv. = 57%; CO = 0.02 vol.%	[99]
Cu/ZrO ₂ (Cu/Zr = 4 mol/mol)	MSR	Oxalate gel co-precipitation	S/C = 1.3; T = 260 °C	Prod. H ₂ = 350 mmol g _{cat} ⁻¹ h ⁻¹ Conv. = 100%; CO = trace amount	[71]
Cu/ZrO ₂ /CeO ₂ (15 mol % CuO)	MSR	Co-precipitation	S/C = 1.0; T = 220 °C	Prod. H ₂ = 0.38 mmol g _{cat} ⁻¹ h ⁻¹ Conv. = 40%; CO = -	[91]
Cu/t-ZrO ₂ (10 wt % Cu)	MS	Complexation with citric acid	P = 80 bar; T = 250 °C	Prod. MeOH = 632 mmol g _{cat} ⁻¹ h ⁻¹ Conv. = 15%; Sel. CO = 14%	[9]
Cu ₁ Zr _{0.5} /SiO ₂ (6.11 wt % Cu)	MS	Control Surface Reaction (CSR)	P = 30 bar; T = 250 °C	Prod. MeOH = 4 mmol g _{cat} ⁻¹ h ⁻¹ Conv. = -;	[3]
Cu/a-Zr _{0.9} @SiO ₂ (4.11 wt % Cu)	MS	Grafting	P = 25 bar; T = 230 °C	Prod. MeOH = 131 mmol g _{cat} ⁻¹ h ⁻¹ Conv. = -%; Sel. CO = -%	[30]
Cu/a-ZrO ₂ (8 wt % Cu)	MS	Incipient wetness	P = 10 bar; T = 230 °C	Prod. MeOH = 1.4 mmol g _{cat} ⁻¹ h ⁻¹ Conv. = -%; Sel. CO = -%	[81]
Cu/a-ZrO ₂ -SiO ₂ (13.7 wt % Cu)	MSR	Incipient wetness	S/C = 1.3; T = 260 °C	Prod. H ₂ = 370 mmol g _{cat} ⁻¹ h ⁻¹ Conv. = 73%; CO = trace amount	[4]

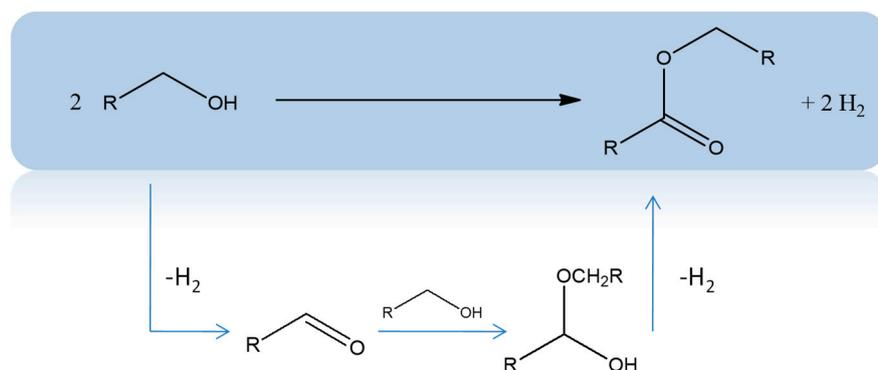
4. Copper–Zirconia Catalysts for the Dehydrogenative Coupling Reaction

Thanks to the recent strong improvements in the bioalcohols production technologies, bioethanol and biobutanol are being produced in ever-increasing amounts from the fermentation of different biomasses—which is better if they are non-food ones [101–103]. Moreover, the use engineered micro-organisms is currently under research for the biological production (fermentation or biosynthesis) of higher alcohols from renewable sources, such in the case of bio-pentanol [104].

In this context, the reactions exploiting (bio)alcohols as starting materials are gaining always more scientific and technical importance to produce a large variety of added-value chemicals [101].

The acceptorless dehydrogenative coupling (DHC) is one of those reactions that allows one to directly transform two molecules of alcohol into the corresponding symmetrical ester, along with the production of two molecules of H₂ (Scheme 1). It is a very attractive green strategy with a very high atom economy since the only “side product”, that is hydrogen, can be easily recovered from the

reaction. The traditional protocols for the preparation of esters on a large scale mainly rely on the use of the corresponding carboxylic acids and homogeneous catalysts, generating a significant amount of waste. The acid-catalyzed Fischer esterification is the most widespread example.



Scheme 1. Dehydrogenative coupling (DHC) process via hemiacetal route.

The DHC process involves sequential absorption/activation, dehydrogenation, and coupling steps. First, the alcohol has to be dissociatively adsorbed on the catalyst surface as alkoxide; then, by dehydrogenation, an aldehydic intermediate is formed. At the same time, hydride species are formed and generate molecular hydrogen. The activated aldehyde is prone to a nucleophilic attack of a second alcohol molecule to give the product of condensation (the hemiacetal). Finally, the dehydrogenation of the hemiacetal leads to the ester and the formation of a second H_2 molecule (Scheme 1) [5,39,105].

This is the widely accepted mechanism operating over heterogeneous catalysts, whereas the alternative pathway of aldehyde dimerization (Tishchenko reaction) is rarely invoked [106,107].

Despite the attractiveness of the DHC process, few heterogeneous catalytic materials are present in the literature. One of the most studied systems is a complex multifunctional catalyst based on zirconia. This is because the reaction requires the co-presence of acid–base pairs for the evolution and the coupling of the alcohol, and a metallic site for the hydride and molecular hydrogen formation. Hence, zirconia has to be coupled with a metal to design an active catalyst and, following the works published, copper seems to be its best partner.

One of the first works reporting the production of ethyl acetate from ethanol in significant yields is operated over a mixed Cu-Zr-Zn-Al system [108]. By performing the reaction feeding only acetaldehyde under N_2 without observing the formation of ethyl acetate, the authors have strongly proved that the reaction proceeds through the hemiacetal route rather than via Tishchenko coupling. The catalytic system has been further improved by acting on the acid–base properties [109]. In particular, a treatment with an alkaline carbonate solution suppresses the acid sites formed upon reduction, which accounts for the formation of the by-products. The work emphasizes the need to control the acidity of the catalyst, but the characterization of the surface acid–base properties of the material prior and after the reduction is lacking. The effect of the basic treatment has been suggested by reactivity tests and by the analysis of the reaction products. However, the same authors have pointed to the role of acid site in favoring also the formation of ethyl acetate by promoting the hemiacetal intermediate. In principle, this means that the decrease in acidity should affect the formation of both the side product(s) and the desired ester. A better discussion on the specific role of the different acidic sites (Lewis and Brønsted) might be helpful in the interpretation of the results. In the same work, the authors have highlighted that the formation of the alkoxide is driven by basic sites by favoring the abstraction of the proton from ethanol. Only a following study shows the decisive effect on the ester formation of the basic sites [40], giving to them an even higher importance than the acid sites. Zirconia, bearing both acid and basic functionalities, promotes the formation of ethyl acetate when added as a mechanical mixture to a Cu/ZnO/Al₂O₃ or PdO/m-ZrO₂ catalyst. The interphase between the Cu- or Pd-based catalyst

and ZrO_2 is extremely relevant for spillover phenomena—that is, the migration of the active species between the two catalytic surfaces.

The zirconia phase has also a great influence on the oxidation state of copper, together with the catalyst preparation method, but a clear trend in this respect is difficult to be define because, as already discussed previously, too many variables are involved, such as the use of additives, dopants or co-oxides, a specific calcination temperature, and reduction procedure.

Often, a copper phase with the co-presence of multiple oxidation states (Cu^+ and Cu^0) is found to be present after a reduction treatment [19,110]. This is only the starting point, which could easily evolve during the reaction. The oxidation state of copper and its catalytic implications are not of easy understanding, and it is often a matter of large debate. Indeed, some authors have shown that the proper combination of Cu^+ and Cu^0 a- ZrO_2 or m- ZrO_2 is beneficial for the DHC reaction [19] but, at the same time, a Cu^{2+} -based catalyst (CuO/ZrO_2) has been found to be extremely active [5], as well as one featuring metallic copper [3].

It is acknowledged that between Cu and Zr, a great interaction is established, especially when high surface area and/or amorphous zirconia is used. This strong interaction drives the metal dispersion, its reducibility, and the formation of Cu–Zr interphase properties that can be properly exploited to design very active catalysts. The interaction between copper and zirconia can be investigated through TPR (temperature-programmed reduction) analysis, whereby small Cu nanoparticles in strong interaction with the support reduce easier than larger and less-interacting aggregates [4,5,19,56,71,99,111–115].

An attempt to provide a direct correlation between interfacial Cu–Zr sites and the activity of these materials in ethyl acetate synthesis has been made by preparing catalysts with a different Zr loading starting from a common benchmark of Cu/SiO_2 [3]. Moderate ester selectivity has been obtained only in the presence of accessible Cu–Zr entities, but the work does not address the nature of the active site.

The cooperative role of copper and zirconia in the DHC reaction has been further elucidated through the absorption of 1-butanol over CuO/ZrO_2 and ZrO_2 surfaces [5]. The FT-IR analyses have shown that the alkoxide is formed on the zirconia, but its further transformation occurs only in the presence of copper. The reported catalyst that exploits a commercial high-surface area a- ZrO_2 is highly active and selective thanks to a high Zr–Cu interdispersion that ensures an elevated presence of active sites. Indeed, the reaction occurs on the acid–base pairs, formed by CuO Lewis acid sites [21,22] and ZrO_2 -based strong basic sites (Figure 7). A yield of 87% of ethyl acetate has been obtained in a solvent-less, gram-scale reaction. By using other linear aliphatic alcohols, an even higher yield has been achieved [5].

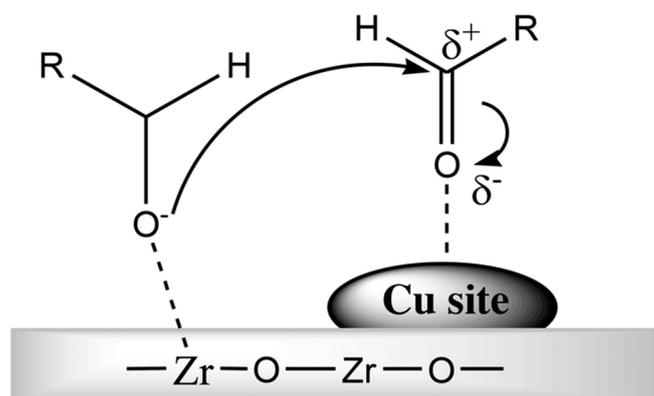


Figure 7. Suggested active site for the DHC reaction in which the acid–base pair is formed by a CuO Lewis acid site and ZrO_2 -based strong basic site. CuO promotes the dehydrogenation of the alcohol and activates the aldehyde towards the attack of a second alcohol molecule activated by the basic sites of ZrO_2 [5]. Reproduced by permission of The Royal Society of Chemistry.

A strong relationship between acid–base pairs and ester yield has been found in a series of copper-based catalysts in which Cu/ZrO₂ stands out for both the investigated parameters [39] (Figure 8). For comparison, the material of the series with the highest number of acid sites, that is the Cu/Al₂O₃, shows an ester yield below 10%, while on Cu/ZrO₂ it is more than 70%. In this case, the site for the reaction is suggested to be constituted by surface acid–base pairs with adjacent metallic Cu species, acting in a synergistic way. Thus, differently to what some of us reported [5], the authors ascribed to copper phase only the dehydrogenation activity and not the acidic one.

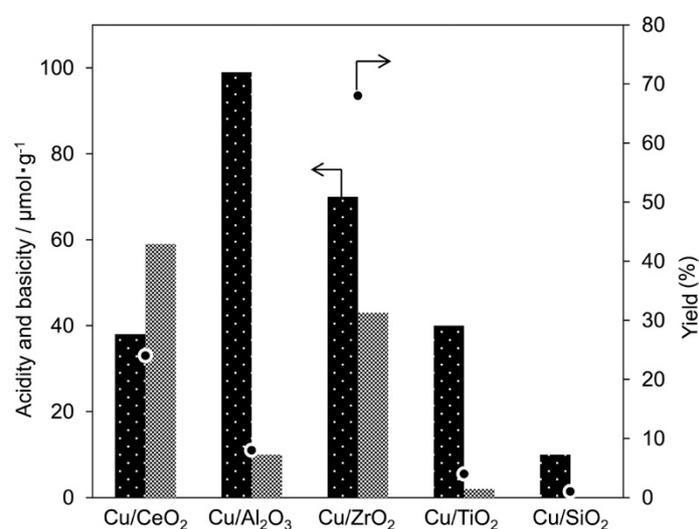


Figure 8. Relationship between the amount of acid (white squares with black background) and base (chessboard pattern) of different catalysts and their octyl octanoate yield (●) [39] (<https://pubs.acs.org/doi/10.1021/acsomega.7b01142>). Reprinted with the permission of the American Chemical Society; further permissions related to the material excerpted should be directed to the ACS.

Few examples on the use of metals others than copper have been reported for the acceptorless DHC reaction [105,116–118]. However, the strong synergy between Cu and Zr has become even more clear with the testing of different supported ZrO₂ materials: Co, Ni, Ru, Pd, Ag, Ir, or Pt catalysts have all exhibited lower activity and selectivity compared to Cu [39].

The high activity of the Cu/ZrO₂ systems makes it unsuitable when highly reactive aromatic alcohols are used. This is because the rapid formation of the aldehyde limits the amount of the alcohol available for the coupling reaction to form the hemiacetal; thus, a limited ester yield can be obtained [39]. For comparison, a Cu/CeO₂ catalyst with a moderate activity in alcohol dehydrogenation has a higher yield of ester on aromatic substrates.

The heterogeneously catalyzed DHC reaction has been studied in particular for the synthesis of linear ester from ethanol and also from different bioalcohols, as they are (always) easily available. This process can be also used for the construction of C–O, C–N, C–S, C–C, and C=C bonds and cyclic compounds, such as lactones [119,120], especially over Pd, Pt, or Ru catalytic systems, different from the Cu–Zr duo.

To the best of our knowledge, despite the improvements in the DHC processes and the promising applications on the large scale, they still remain in the lab-scale research, and no industrial use is currently operating. In Table 2, we summarize the catalytic behavior for the Cu-, Zr-based catalysts in DHC reaction.

Table 2. Comparison between the different Cu-, Zr-based catalysts in DHC reaction.

Catalyst	Substrate	Condition	T (°C)	C (%)	S (%)	Ref.
Cu-Zn-Zr-Al-O	Ethanol	Gas phase	240	82	76	[108]
Cu/m-ZrO ₂	Ethanol	Gas phase	300	49	81	[19]
Cu/m-ZrO ₂	Ethanol	Gas phase	200	45	73	[100]
Cu/ZrO ₂ /Al ₂ O ₃	Ethanol	Gas phase	260	86	71	[121]
Cu ₁ Zr _{0.25} /SiO ₂	Ethanol	Gas phase	200	30	33	[3]
Cu-Zn-Zr-Al-O	Ethanol	Gas phase	220	66	85	[99]
Cu/a-ZrO ₂	Ethanol	Batch	250	89	98	[5]
Cu/a-ZrO ₂	1-butanol	Batch	250	98	100	[5]
Cu/m-ZrO ₂	1-octanol	Batch	170	99	68	[39]
Cu-Zn-Zr-Al-O	1,4-butanediol	Gas phase	240	84	98	[110]

5. Challenges and Perspectives

Copper-zirconia are extremely versatile and tunable materials. Redox and acid-base properties can be controlled by the right combination of zirconia and copper, leading to a multifunctional catalyst. Due to the complexity of the system, which is simple only in its appearance, different parameters must be controlled during the synthesis, making a comparison and a systematic rationalization of its properties fairly hard.

Table 3 tentatively lists the main milestones on the comprehension of the copper-zirconia systems by using methanol economy-related reactions and the DHC reaction as case histories.

Table 3. Significant advances in the comprehension of copper-zirconia catalysts (MS = methanol synthesis; MSR = methanol steam reforming; MD = methanol decomposition; DHC = dehydrogenative coupling reaction)

Reaction	Focus	Significant Advances	Year	Ref.
DHC	Deep study of the reaction products and intermediates	Strong evidences of the hemiacetal mechanism as the active one	2002	[108]
MSR	Study on the actual active phase	Evidences of Cu ⁺ role in promoting the reaction	2005	[78]
MSR	Study on the actual active phase	Insights on the cooperative action of Cu ⁰ and Cu ⁺ sites	2006	[99]
MSR	Correlation between exposed Cu phase and activity	No linear correlation found	2006	[71]
MSR	Study on the reaction mechanism	Two distinct catalytic sites: one for dehydrogenation and one for molecular hydrogen formation	2007	[91]
DHC	Use of mechanical mixture of different catalysts	Awareness on the role of the basic site	2010	[40]
MS	Impact of the crystal phases on the activity	Oxygen vacancies formation on t-ZrO ₂ result in abundant Lewis acid sites in the form of Cu ⁺ sites	2014	[9]
MSR	Role of Cu-Zr interphase	Evidences on the role of Cu/ZrO _x H phase boundaries on the activity	2015	[29]
DHC/MS	Synthesis of well-defined Cu-Zr catalysts.	Further emphasis on the Cu-Zr interphase for the activity	2016	[3]
DHC	Use of high SA zirconia and the preparation a catalyst with high Cu-Zr interdispersion	Elucidation on the cooperative role between Zr and Cu in promoting the reaction	2017	[5]
DHC	Comparison between Cu-based catalysts with different acid-base properties	Strong correlation between acid-base pairs and activity	2017	[39]
MD	Elucidation of Cu ⁰ and Cu ⁺ roles in methanol dehydrogenation	Cu ⁺ sites responsible for the final CO formation from the intermediates on Cu ⁰ sites, on which cleavage of the C-H and O-H bonds occur	2018	[69]
MS	Role of Zr sites	<i>cus</i> Zr (IV) sites act as Lewis acids and assist the CO ₂ activation Oxygen vacancies no longer critical	2018	[30]
MS	Maximization of the Cu-Zr interphase	Cu _x Zr _y O _z phase maximizes the Cu-Zr interaction and is favoured on a-ZrO ₂	2018	[2,81]
MSR	Maximization of Cu active phase	Electron-poor metallic Cu nanoparticles act as <i>all-in-one</i> active site	2019	[4]

The extensive and systematic study carried out so far has undoubtedly deepened our understanding of such systems in the two broad fields discussed in this review. Reaction mechanisms have been linked to the actual catalytic sites present under reaction conditions, eventually identifying the most relevant descriptors of the overall process. These insights are revealing to be precious for the

exploitation of copper–zirconia catalysts in new fields owing to multifunctionality. One example is the transformation of substrates derived from cellulose or hemicellulose, such as levulinic acid and γ -valerolactone [8,31,43,44,122–126], which is certainly an emerging trend due to the need to improve the efficiency and the sustainability of the transformation routes of lignocellulose valorization for the production of strategic platform molecules and valuable compounds.

More in detail, after many years of research, it turned out that the most impacting aspects of the copper zirconia catalysts are two: the copper exposure, and hence the copper–zirconia interphase, and the zirconia surface hydroxylation degree, which is tightly connected to the acid–base properties. Their optimization has direct implications on the surface hydrogen and intermediates mobility and on the electronics and stability of the copper phase. High surface area zirconia, with the α -ZrO₂ being highly promising, and high amounts of exposed *cus* Zr (IV) sites, that act as Lewis centers and therefore help hydrogenating/dehydrogenating the intermediates, are effective tools to achieve high catalytic activity (Figure 1). The role of the oxygen vacancies seems to be less critical than what was once believed and mainly consists in promoting the Cu⁺ formation. Their population depends on the crystallographic phase and the presence of the proper dopant.

The high activity of ZrO₂ in catalytic transfer hydrogenation reactions [127–129] makes it a powerful means for the development of H₂-free cascade processes in the biorefinery scenario, and the combination with copper allows the design of innovative multifunctional materials. In this sense, the versatility of zirconia-based catalysts is evident in the methanol synthesis whereby ZnO can convert only CO₂, whereas the acid–base pairs of ZrO₂ permit also the hydrogenation of CO [52].

Copper–zirconia are also systems with low environmental impact. The European Medicine Agency classification shows how copper has very low toxicity with respect to noble metals and Ni, while ZrO₂ is considered to be a safe material [130,131].

The most significant drawbacks still hampering the implementation on the industrial scale are the fine control over the phase composition of the zirconia, with relevant consequences on both the availability and stability of the copper phase, and the precise tuning of the acid–base properties, which is still quite elusive. All this is further complicated by the fact that typically zirconia-base materials have a dynamic behavior under reaction conditions, such as copper aggregation, loss, and/or changes in its oxidation state, making the overall stability of the catalyst the first issue that still requires effective answers.

6. Conclusions

Even though the comprehension of copper–zirconia systems has reached a deep level and the catalysts have shown high activity in the methanol economy, in our view, their full potential is still to be exploited, especially as far as the transformation of biomass-derived platform molecules to high added-value products is concerned. In this sense, new applications are growing, especially for what concerns the valorization of the platform molecules that derive from lignocellulose stream, but these still remain largely unexplored fields.

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