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.

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 synthetized (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](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, synthetizing a catalyst with around 60% of dispersion and
a final surface area of 216 m$^2$/g (before copper deposition, it was 309 m$^2$/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 H$_2$) before the reaction. Depending on the application, one may need to stabilize Cu$^{2+}$, 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 CO$_2$ (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 CO$_2$ 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 CO$_2$ 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].

\[
\begin{align*}
\text{CO}_2 + 3\text{H}_2 & = \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \text{MS} \quad \Delta H_{298K} = -49.7 \text{ kJ/mol} \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & = \text{CO}_2 + 3\text{H}_2 \quad \text{MSR} \quad \Delta H_{298K} = +49.7 \text{ kJ/mol} \\
\text{CH}_3\text{OH} & = \text{CO} + 2\text{H}_2 \quad \text{MD} \quad \Delta H_{298K} = +90.2 \text{ kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & = \text{CO}_2 + \text{H}_2 \quad \text{WGS} \quad \Delta H_{298K} = -41.2 \text{ kJ/mol}
\end{align*}
\]

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].

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 CO$_2$ conversions can be obtained in the MS reaction because CO$_2$ 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 Zr$^{3+}$ 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/SiO$_2$ [4], zirconia promotes the Cu reducibility in general, and specifically, Cu on t-ZrO$_2$ reduces at lower temperature than on m-ZrO$_2$. 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 CO$_2$ 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 CO$_2$ (or CO) and H$_2$ in the former, and of methanol and water in the latter. The direct synthesis from CO$_2$ 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/ZrO$_2$ 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 CO$_2$ 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. CO$_2$ adsorbs on the zirconia and then is readily transformed into carbonates [62], while with CO, hydroxylated Zr sites adjacent to coordinatively unsaturated (cus) Zr$^{4+}$ 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-ZrO$_2$ phase has been reported to adsorb more CO$_2$ than the t-ZrO$_2$ because of the higher concentration of basic O$^{2-}$ sites and cus Zr$^{4+}$ Lewis acid sites. Hence, one might think that m-ZrO$_2$ 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 CO$_2$ are obtained with t-ZrO$_2$. 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-ZrO$_2$, 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/CO$_2$/H$_2$ mixture [6], which is possible thanks to the activity of Cu in the WGS reaction that facilitates the conversion of CO into CO$_2$. 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-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-ZrO$_2$, Tada et al. [2,81] reported as more selective to methanol a catalyst prepared on a-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 (Cu$_x$Zr$_y$O$_{2x+y}$). This, along with the weaker adsorption of methanol on a-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.

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
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 catalysts.

High atom economy since the only “side product”, that is hydrogen, can be easily recovered from the production of two molecules of H₂.

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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
<th>Preparation Procedure</th>
<th>Reaction Conditions</th>
<th>Catalytic Performances</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZrO₂ (80 wt % Cu)</td>
<td>MSR</td>
<td>Co-precipitation</td>
<td>$%C = 1.5; T = 250 ^\circ C$</td>
<td>Prod. H₂ = 400 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} Conv. = -; Sel. CO &lt; 0.1%</td>
<td>[78]</td>
</tr>
<tr>
<td>Cu/\textit{t}- and m-ZrO₂ (15 wt % Cu)</td>
<td>MSR</td>
<td>Microemulsion technique</td>
<td>$%C = 1.0; T = 250 ^\circ C$</td>
<td>Prod. H₂ = -; Conv. = 57%; CO = 0.02 vol.%</td>
<td>[99]</td>
</tr>
<tr>
<td>Cu/ZrO₂ (Cu/Zr = 4 mol/mol)</td>
<td>MSR</td>
<td>Oxalate gel co-precipitation</td>
<td>$%C = 1.3; T = 260 ^\circ C$</td>
<td>Prod. H₂ = 350 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} Conv. = 100%; CO = trace amount</td>
<td>[71]</td>
</tr>
<tr>
<td>Cu/ZrO₂/Co₂ (15 mol % CuO)</td>
<td>MSR</td>
<td>Co-precipitation</td>
<td>$%C = 1.0; T = 220 ^\circ C$</td>
<td>Prod. H₂ = 0.38 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} Conv. = 40%; CO = -</td>
<td>[91]</td>
</tr>
<tr>
<td>Cu/\textit{t}-ZrO₂ (10 wt % Cu)</td>
<td>MS</td>
<td>Complexation with citric acid</td>
<td>P = 80 bar; T = 250 ^\circ C</td>
<td>Prod. MeOH = 632 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} Conv. = 15%; Sel. CO = 14%</td>
<td>[9]</td>
</tr>
<tr>
<td>Cu/\textit{a}-ZrO₂/SiO₂ (6.11 wt % Cu)</td>
<td>MS</td>
<td>Control Surface Reaction (CSR)</td>
<td>P = 30 bar; T = 250 ^\circ C</td>
<td>Prod. MeOH = 4 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} Conv. = -</td>
<td>[3]</td>
</tr>
<tr>
<td>Cu/\textit{a}-ZrO₂/SiO₂ (4.11 wt % Cu)</td>
<td>MS</td>
<td>Grafting</td>
<td>P = 25 bar; T = 220 ^\circ C</td>
<td>Prod. MeOH = 131 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} Conv. = -; Sel. CO = 5%</td>
<td>[30]</td>
</tr>
<tr>
<td>Cu/\textit{a}-ZrO₂ (8 wt % Cu)</td>
<td>MS</td>
<td>Incipient wetness</td>
<td>P = 10 bar; T = 230 ^\circ C</td>
<td>Prod. MeOH = 1.4 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} Conv. = -; Sel. CO = 5%</td>
<td>[61]</td>
</tr>
<tr>
<td>Cu/\textit{a}-ZrO₂-SiO₂ (13.7 wt % Cu)</td>
<td>MSR</td>
<td>Incipient wetness</td>
<td>$%C = 1.3; T = 260 ^\circ C$</td>
<td>Prod. H₂ = 370 mmol g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} Conv. = 73%; CO = trace amount</td>
<td>[4]</td>
</tr>
</tbody>
</table>

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.](image)

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 H₂ 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 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 N₂ without observing the formation of ethyl acetate, the authors have strongly proved that the reaction proceeds though 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 proprieties 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.](image-url)
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.

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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate</th>
<th>Condition</th>
<th>T (°C)</th>
<th>C (%)</th>
<th>S (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–Zn–Zr–Al–O</td>
<td>Ethanol</td>
<td>Gas phase</td>
<td>240</td>
<td>82</td>
<td>76</td>
<td>[108]</td>
</tr>
<tr>
<td>Cu/m-ZrO₂</td>
<td>Ethanol</td>
<td>Gas phase</td>
<td>300</td>
<td>49</td>
<td>81</td>
<td>[19]</td>
</tr>
<tr>
<td>Cu/m-ZrO₂</td>
<td>Ethanol</td>
<td>Gas phase</td>
<td>200</td>
<td>45</td>
<td>73</td>
<td>[100]</td>
</tr>
<tr>
<td>Cu/ZrO₂/Al₂O₃</td>
<td>Ethanol</td>
<td>Gas phase</td>
<td>260</td>
<td>86</td>
<td>71</td>
<td>[121]</td>
</tr>
<tr>
<td>Cu₁Zr₀.₂₅/SiO₂</td>
<td>Ethanol</td>
<td>Gas phase</td>
<td>200</td>
<td>30</td>
<td>33</td>
<td>[3]</td>
</tr>
<tr>
<td>Cu-Zn-Zr-Al-O</td>
<td>Ethanol</td>
<td>Gas phase</td>
<td>220</td>
<td>66</td>
<td>85</td>
<td>[99]</td>
</tr>
<tr>
<td>Cu/a-ZrO₂</td>
<td>Ethanol</td>
<td>Batch</td>
<td>250</td>
<td>89</td>
<td>98</td>
<td>[5]</td>
</tr>
<tr>
<td>Cu/a-ZrO₂</td>
<td>1-butanol</td>
<td>Batch</td>
<td>250</td>
<td>98</td>
<td>100</td>
<td>[5]</td>
</tr>
<tr>
<td>Cu/m-ZrO₂</td>
<td>1-octanol</td>
<td>Batch</td>
<td>170</td>
<td>99</td>
<td>68</td>
<td>[39]</td>
</tr>
<tr>
<td>Cu–Zn–Zr–Al–O</td>
<td>1,4-butanediol</td>
<td>Gas phase</td>
<td>240</td>
<td>84</td>
<td>98</td>
<td>[110]</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Focus</th>
<th>Significant Advances</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHC</td>
<td>Deep study of the reaction products and intermediates</td>
<td>Strong evidences of the hemiacetal mechanism as the active one</td>
<td>2002</td>
<td>[108]</td>
</tr>
<tr>
<td>MSR</td>
<td>Study on the actual active phase</td>
<td>Evidences of Cu⁺ role in promoting the reaction</td>
<td>2005</td>
<td>[78]</td>
</tr>
<tr>
<td>MSR</td>
<td>Study on the actual active phase</td>
<td>Insights on the cooperative action of Cu⁰ and Cu⁺ sites</td>
<td>2006</td>
<td>[99]</td>
</tr>
<tr>
<td>MSR</td>
<td>Correlation between exposed Cu phase and activity</td>
<td>No linear correlation found</td>
<td>2006</td>
<td>[71]</td>
</tr>
<tr>
<td>MSR</td>
<td>Study on the reaction mechanism</td>
<td>Two distinct catalytic sites: one for dehydrogenation and one for molecular hydrogen formation</td>
<td>2007</td>
<td>[91]</td>
</tr>
<tr>
<td>DHC</td>
<td>Use of mechanical mixture of different catalysts</td>
<td>Awareness on the role of the basic site</td>
<td>2010</td>
<td>[40]</td>
</tr>
<tr>
<td>MS</td>
<td>Impact of the crystal phases on the activity</td>
<td>Oxygen vacancies formation on t-ZrO₂ result in abundant Lewis acid sites in the form of Cu⁺ sites</td>
<td>2014</td>
<td>[9]</td>
</tr>
<tr>
<td>MSR</td>
<td>Role of Cu-Zr interphase</td>
<td>Evidences on the role of Cu₅ZrO₅H phase boundaries on the activity</td>
<td>2015</td>
<td>[29]</td>
</tr>
<tr>
<td>DHC/MS</td>
<td>Synthesis of well-defined Cu-Zr catalysts</td>
<td>Further emphasis on the Cu-Zr interphase for the activity</td>
<td>2016</td>
<td>[3]</td>
</tr>
<tr>
<td>DHC</td>
<td>Use of high SA zirconia and the preparation a catalyst with high Cu-Zr interdispersion</td>
<td>Elucidation on the cooperative role between Zr and Cu in promoting the reaction</td>
<td>2017</td>
<td>[5]</td>
</tr>
<tr>
<td>DHC</td>
<td>Comparison between Cu-based catalysts with different acid–base properties</td>
<td>Strong correlation between acid–base pairs and activity</td>
<td>2017</td>
<td>[39]</td>
</tr>
<tr>
<td>MD</td>
<td>Elucidation of Cu⁰ and Cu⁺ roles in methanol dehydrogenation</td>
<td>Strong correlation relationship between acid-base pairs and activity</td>
<td>2018</td>
<td>[69]</td>
</tr>
<tr>
<td>MS</td>
<td>Role of Zr sites</td>
<td>Cu⁺ sites responsible for the final CO formation from the intermediates on Cu⁰ sites, on which cleavage of the C-H and O-H bonds occur</td>
<td>2018</td>
<td>[30]</td>
</tr>
<tr>
<td>MS</td>
<td>Maximization of the Cu-Zr interphase</td>
<td>CuxZr5O₅ phase maximizes the Cu-Zr interaction and is favoured on a-ZrO₂</td>
<td>2018</td>
<td>[2,61]</td>
</tr>
<tr>
<td>MSR</td>
<td>Maximization of Cu active phase</td>
<td>Electron-poor metallic Cu nanoparticles act as all-in-one active site</td>
<td>2019</td>
<td>[4]</td>
</tr>
</tbody>
</table>

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-ZrO$_2$ being highly promising, and high amounts of exposed $\text{CuO}_\text{Zr}$ (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 ZrO$_2$ in catalytic transfer hydrogenation reactions [127–129] makes it a powerful means for the development of H$_2$-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 CO$_2$, whereas the acid–base pairs of ZrO$_2$ 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 ZrO$_2$ 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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