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# Microstructural and Chemical Evolution and Analysis of a Self-Activating CO<sub>2</sub>-Selective Cu-Zr Bimetallic Methanol Steam Reforming Catalyst

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#### Abstract

The microstructure of the CO<sub>2</sub>-selective self-activating and self-stabilizing Cu-Zr bimetallic compound Cu<sub>51</sub>Zr<sub>14</sub> has been studied by a combination of high-resolution electron microscopy and energy-dispersive X-ray spectroscopy both before and after entering the CO<sub>2</sub> selective state in methanol steam reforming. Prior to catalysis, the phase composition of the catalyst is characterized by a microstructural mixture of Cu<sub>51</sub>Zr<sub>14</sub> and metallic Cu. The structure appears in a distinct needle-like morphology with a characteristic microstucture of small Cu particles embedded in the intermetallic matrix. In contrast, entering the CO<sub>2</sub>-selective state goes along with oxidative decomposition - investigated by differential thermal analysis (DTA), thermogravimetry (TG) and mass spectrometry (MS) - and therefore massive structural and compositional changes of the Cu<sub>51</sub>Zr<sub>14</sub> compound both in the near-surface and bulk regions. The final state is then composed of a structurally very heterogeneous sample with Zr-rich and Cu-rich regions within the material bulk with a characteristic lamellar structure. Most importantly, the catalytically relevant surface regions are drastically corroded and depleted in Zr and are characterized by a majority of Cu in intimate contact with oxidized ZrO<sub>2</sub> exhibiting a well-ordered, predominantly tetragonal structure. This newly created Cu-ZrO<sub>2</sub> interface is believed to be the most significant descriptor steering the CO<sub>2</sub> selectivity. In due course, the new way of self-adjustment of the microstructure starting from well-defined intermetallic compounds in the catalytic reaction mixture might pave the way for a more systematic approach of controlled oxidative decomposition of intermetallic compounds acting as promising catalyst precursors.

#### **1. Introduction**

Copper-based materials are important catalysts in methanol chemistry with use in methanol synthesis from syngas, CO<sub>2</sub> hydrogenation to produce renewable methanol or methanol steam reforming (MSR).<sup>1</sup> Tunable and reproducible steering of the product selectivity is a prerequisite for technical applications. For MSR the important parameters include high CO<sub>2</sub> selectivity, low CO content and maximum  $H_2$  yield<sup>2</sup>. As for the use of  $ZrO_2$  in the methanol steam reforming reaction, addition of ZrO2 to Cu/ZnO catalysts allows suppressing the poor sintering stability of the latter<sup>2</sup>. Similar beneficial and synergistic effects have also been described both for Cu/Zn and complexer Cu/Zn/Al materials in methanol synthesis<sup>3</sup>. Synergistic Cu-ZrO<sub>2</sub> interactions have similarly been reported for pure Cu/ZrO<sub>2</sub> catalysts, exhibiting direct Cu-O-Zr bonds at the phase boundary. These interactions are considered to play a key role in steering the methanol reforming selectivity to maximum CO<sub>2</sub> yield<sup>4</sup>. A nanocrystalline Cu/tetragonal ZrO<sub>2</sub> catalyst was already reported to be particularly promising in terms of activity, selectivity and stability especially with respect to a technically used  $Cu/ZnO/Al_2O_3$  methanol synthesis catalyst<sup>5,6</sup>. Efforts to explain the high selectivity have been considerable and are mainly centered at around two important beneficial parameters: the redox chemistry of Cu at the interface and structural properties within the metallic Cu phase (such as defects or disordered phases)<sup>2</sup>. However, the situation is far from being clear, since both beneficial<sup>4,7,8</sup> and detrimental<sup>9</sup> effects of Cu reducibility are equally reported. Apart from the role of Cu, also the role of the ZrO<sub>2</sub> polymorph has been controversly discussed. Mostly, its tetragonal modification has been reported to have a beneficial impact on the catalytic properties of Cu-ZrO<sub>2</sub> or Ag-ZrO<sub>2</sub> systems (e.g. in methanol synthesis or CO<sub>2</sub> hydrogenation).<sup>10-16</sup> However, also a positive influence of monoclinic ZrO<sub>2</sub> has been discussed in methanol synthesis.<sup>17,18</sup> As for the role of tetragonal ZrO<sub>2</sub>, the stabilization of ionic Cu species and the tetragonal structure itself by oxygen vacancies has been held accountable for the beneficial effects. Despite the contradicting information, especially the chemical composition (i.e. the reversible partially hydroxylated  $ZrO_xH_y$  sites) of the *in situ* formed Cu-ZrO<sub>2</sub> interfacial sites are most important. This is important insofar as the oxidic entity of such a catalyst may synergistically participate in the reaction in two ways: (i) by stabilizing oxygenate intermediates or (ii) by directly activating water<sup>2</sup>. The latter has already been identified on the corresponding Pd-ZnO<sup>19-21</sup> and Cu-ZnO<sup>22</sup> catalysts as the most important step in CO<sub>2</sub>-selective methanol steam reforming.

Apart from the conventional impregnated catalysts, also different pre-cursor materials have been studied. One important class of materials, which are directly related to the work presented here and which have also been studied in a number of reactions, are Cu-Zr amorphous glassy alloys. However, these alloy phases suffer the significant drawback of being not very active and selective in e.g. CO<sub>2</sub> hydrogenation<sup>23</sup>, partial oxidation of alcohols<sup>24</sup> or in methanol synthesis<sup>25,26</sup>, as long as they are not deliberately doped with other noble metals (e.g. Au or Pd) and/or activated by O<sub>2</sub> or air. This obviously further complicates the elucidation of the active and selective state<sup>27,28</sup>.

We have recently reported not only on the structural and chemical steering effects of Cu-ZrO<sub>2</sub> catalysts prepared by different synthesis routines to identify the complex structural prerequisites for CO-, CO<sub>2</sub>,- and formaldehyde-selective methanol steam reforming<sup>29,30</sup>, but also exemplified the surprisingly high activity and extremely high selectivity of a bimetallic Cu/Cu<sub>51</sub>Zr<sub>14</sub> pre-catalyst, *in situ* decomposed via contact to the MSR reaction mixture<sup>31</sup>. In this case, CO<sub>2</sub>-selective reaction channels were controlled by the resulting Cu-ZrO<sub>2</sub> interface, suppressing full dehydrogenation of methanol to CO *and* subsequently promoting the total oxidation of intermediate oxygenates to CO<sub>2</sub> by water. With the new preparation/activation technique, the surface-normalized CO<sub>2</sub> activity was increased by a factor of ~100 in comparison to similar ZnPd<sup>19,20</sup> or CuZn<sup>22</sup> systems. The most crucial outcome was the self-

activating and self-stabilizing state with co-existence of dispersed Cu and partially hydroxylated tetragonal  $ZrO_2$ , responsible for efficient water activation and, consequently, high  $CO_2$  selectivity<sup>31</sup>.

In the present work, we provide an in-depth microscopical and spectroscopic study of the microstructural evolution and DTA/TG/MS analysis of the transition of the Cu/Cu<sub>51</sub>Zr<sub>14</sub> precursor material into the oxidatively decomposed and corroded Cu/tetragonal ZrO<sub>2</sub> state. We will focus on both the surface and bulk structure and composition of the CO<sub>2</sub>-selective state in methanol steam reforming with the ultimate aim of eventually identifying the structural steering effects. The optimum tools to fulfill this task are considered (high resolution) electron microscopy and energy-dispersive X-ray spectroscopy. For the sake of clarity, the first section in the Results and Discussion chapter will give a brief synopsis of the recent catalytic results.

#### 2. Experimental

For preparation of the catalyst pre-cursor, Cu foil (Goodfellow, purity: 99.95 %, thickness: 0.125 mm) and Zr foil (Alfa Aesar, purity: 99.95 %, thickness: 0.127 mm) where piled up in a Ta crucible in a pre-determined atomic ratio of Cu:Zr = 2:1, representing an empirical optimized ratio between Cu and Zr. The maximum content of Zr is limited by the completeness of the reaction between Cu and Zr, since higher Zr contents (i.e. higher than Cu:Zr = 2:1) inevitably lead to Cu-Zr intermetallic/Zr metal admixtures under the applied reaction conditions. Samples with lower Zr contents (e.g. Cu:Zr = 9:2) have been prepared and catalytically characterized. As the activity was generally lower, they have not been further considered for in depth structural analysis. Resistive heating under high vacuum conditions (~1x10<sup>-7</sup> mbar) slightly above the melting temperature of Cu (1360 K) causes the formation of a homogeneous melt via a solid-liquid reaction of solid Zr and molten Cu. Under this experimental conditions, the evaporation of Cu is negligibly low. Controlled cooling to 300 K after the reaction is performed within half an hour with a time-averaged cooling rate of ~30 K

min<sup>-1</sup>. Temperature-programmed methanol steam reforming experiments were performed using an UHV-attached high-pressure batch reactor with continuous MS detection. The following starting conditions were applied: 12 mbar methanol, 24 mbar water, 8 mbar Ar, 956 mbar He. Ar was used for correction of thermal expansion and pressure drop due to gas withdrawal through the capillary leak to the MS. The temperature program was adjusted to 10 K min<sup>-1</sup> temperature ramp up to 623 K and an isothermal period at 623 K for 30 min. The catalyst is then transported via air to TEM analysis. Note that despite the use of Ta as support material, no Ta (or associated Cu-Ta intermixing) has been observed by EDX within the prepared pre-catalyst state.

In general, the microstructure is critical to the catalytic performance and as such, it can be controlled basically in two ways: either by modifying the initial nominal Cu:Zr ratio or by adjusting the composition of the methanol steam reforming feed. Since the latter was not changed because these studies were conducted using a set fixed ratio of methanol:water 1:2 (to avoid the reaction being stopped due to water depletion), the only parameter that has been experimentally varied is the above-mentioned Cu:Zr ratio. All catalysts have been pre-tested catalytically to make sure they give the aimed-for CO<sub>2</sub> selectivity, but since they performed significantly worse than the Cu:Zr ratio 2:1 discussed here, they have not been subjected to the same TEM/SEM in depth analysis. For quality control, repeating the experiments for the catalytically best performing 2:1 = Cu:Zr composition four times (i.e. by controlling the microstructure upon treatment in the methanol steam reforming mixture up to 623 K for four freshly prepared samples), both the resulting microstructure and the obtained CO<sub>2</sub> selectivity are similar.

Elemental and structural analysis was performed by electron microscopy and EDX spectroscopy. The transmission electron microscopic (TEM) investigations were performed using a FEI TECNAI F20 field emission TEM, equipped with a high angle annular dark field

STEM detector (HAADF), an Apollo XLTW SDD X-Ray detector and a GATAN GIF Tridiem image filter. The spatial resolution of the EDX maps is about 1 nm. The TEM samples were prepared by means of focused ion beam (FIB) using a FEI Quanta 200 dual beam FIB and gentle Ar<sup>+</sup>-ion polishing in order to remove beam damage from prior FIB milling. To protect the surface, a Pt covering layer is deposited prior to the FIB process. Further, the layer is cut by using a Ga ionic beam, whose energy is decreased to about 1 kV in the last preparation step. This avoids damage to the cut layer.

For powder X-ray diffraction (PXRD) measurements in transmission, the sample was carefully bended to break off the material from the Ta support. The broken-off material was ground and fixed between two Kapton®-foils with an n-hexane/vaseline mixture. The X-ray powder diffraction patterns were obtained on a Huber image plate G670 with a Cu-K<sub> $\alpha$ 1</sub> source ( $\lambda = 1.54056$  Å) and a quartz monochromator in the range from 3° < 20 < 100°.

Differential thermal analysis/thermogravimetry/mass spectrometry measurements (DTA/TG/MS) were conducted under reaction conditions. Therefore, 38 mg of powdered material was measured in a DTA/TG (Netzsch, STA 449 F3 Jupiter). The specific mass/charge-signals of the outgoing gases were surveyed with a mass spectrometer (Pfeiffer, Omnistar GSD 301 O3). The materials were held under He (40 mL/min) for 30 min to get a stable baseline, and subsequently heated to 423 K with a rate of 5 K/min and held there for 30 min. Then a flow of 0.39 g/h liquid MeOH/H<sub>2</sub>O-mixture (50 mol-% methanol (Sigma Aldrich,  $\geq$  99.9 %), 50 mol-% deionized water) was evaporated at 473 K and added to the gas mixture. After that, the sample was heated to 623 K with 5 K/min, held there for 30 min, cooled to 423 K with 5 K/min held there again for 30 min. This heating and cooling cycle was repeated to investigate if the changes in the sample are reversible. Then the flow of MeOH/H<sub>2</sub>O was stopped and the material was cooled to room temperature. The measurement is background corrected with a blind measurement of the empty Al<sub>2</sub>O<sub>3</sub> crucibles. The samples after the DTA/TG/MS were characterized by powder X-ray diffraction.

For SEM experiments, a FEI Quanta 250 field emission SEM was used. Prior to SEM imaging, the samples were coated with 10 nm Au/Pd to improve their conductance.

#### 3. Results and Discussion

#### 3.1. Short review of catalytic results

For the sake of clarity and to provide the best possible correlation to the discussion about the microstructure, this section provides a very brief account of the so far obtained catalytic results. These have been discussed in detail together with limited structural characterization elsewhere and are also shown as Figure S1 in the Supporting Information<sup>31</sup>. Treatment of the Cu/Cu<sub>51</sub>Zr<sub>14</sub> pre-cursor in a methanol steam reforming mixture (methanol:water = 1:2, 12 and 24 mbar, respectively) up to 623 K led to a highly active and CO<sub>2</sub> selective state with a catalytic light-off temperature at around 550 K after the first cycle. Whereas the CO<sub>2</sub> selectivity remained constantly high (> 99.9%), this light-off temperature with increasing cycle number (4 have been performed in a row) finally shifted to about 470 K after the third and fourth run. During this self-activation steps, the activity of the catalyst doubled from the first to the fourth run. As the most important aspect is the understanding of the high CO<sub>2</sub>-selectivity developing during the structural self-activation, the state discussed in sections 3.3 and 3.4 is the one in the selective state after the first catalytic cycle<sup>31</sup>.

#### 3.2. Morphological and structural state before methanol steam reforming

As the samples were prepared by melting on a Ta crucible, Figure 1 shows optical micrographs of the obtained pre-catalyst before (Figure 1A) and subsequently after entering the  $CO_2$ -selective state (Figure 1B). As evidenced in Figure 1A, (and further shown in Figure S2), the pre-catalyst highlights a distinct needle-like morphology (best visible in the lower

part of the image). This most likely is the result of slowly cooling down the melt to room temperature. The sample – in contrast to the one after treatment in the reaction mixture – exhibits a characteristic metallic gloss. In addition, the sample after treatment does not show this needle-like morphology, already indicating that not only chemical changes, but also a complex structural transition has taken place. This will be discussed in section 3.4. As shown by previously discussed XRD measurements (Figure S3), the pre-catalyst state is composed of a  $Cu_{51}Zr_{14}$  phase in co-existence with metallic Cu in an approximate vol.-% ratio of 72:28<sup>31</sup>. Since the chemical composition of the phase mixture has a higher Cu-content than the starting composition, it is likely that the Zr-richer phase  $CuZr_2$  is present in the sample as expected from the latest phase diagram investigation<sup>32</sup>. However, the latter can not be identified in the powder X-ray diffraction pattern due to overlap with the  $Cu_{51}Zr_{14}$  reflections. Thus, despite the slow cooling, the sample is not in thermodynamic equilibrium. The  $Cu_{51}Zr_{14}$  intermetallic compound possesses a hexagonal  $Ag_{51}Ge_{14}$ -type structure with space group  $P6/m^{33}$ . No other phases (especially oxidized compounds) are present.



**Figure 1:** Optical micrographs of the as-prepared  $Cu_{51}Zr_{14}/Cu$  catalyst pre-cursor on the Ta foil before the methanol steam reforming treatment (A) and after that treatment (methanol:water 1:2, 12 and 24 mbar; maximum reaction temperature 623 K) (B).

The needle-like morphology can be also seen in the corresponding SEM images (Figure S2 A). The needles exhibit diameters of up to 150  $\mu$ m and lenghts up to the mm range. At closer view (Figure S2 B), the structure is composed of extended homogeneous regions with a small-grain structure (best visible in the upper left and lower areas) and in addition by small

enclosed regions with a distinctly different contrast. These structures are both found in bulk regions (lower left corner) and sometimes also penetrate to the surface (which is indicated by the three white arrows). Note already at this stage that the image is derived from a FIB-cut layer perpendicular to the surface. That is, the surface is found on the right, and the bulk of the sample on the left. The grey striped contrast to the right is not part of the intermetallic compound, but due to the Pt cover layer arising from the FIB cut.

To obtain further information about the chemical distribution within the sample, EDX measurements have been carried out. These are highlighted both for surface and bulk regions in Figure 2. Here, the associated TEM overview image (Figure 2A) is shown alongside the respective intensities from the Cu-K (Figure 2B), Zr-K (Figure 2C) and the overlap of Cu-K, Zr-K and O-K (Figure 2D).

As shown in Figure 2A (and Figure S4), the observed TEM contrast is over vast regions, also deep inside the sample bulk, homogeneous. This is now directly corroborated by the EDX measurements, which reveal an almost even and homogeneous Cu and Zr distribution within this structure. This, thus, directly proves that these are the regions where the  $Cu_{51}Zr_{14}$  intermetallic is predominantly found. Additionally, the EDX analysis also reveals that the islands enclosed within the homogenous matrix (cf. Figure 2B) are not only clearly enriched in Cu, but in fact consist almost entirely of metallic Cu. These islands, as derived from the XRD measurements previously and now directly proven also by TEM and EDX, are consequently the minority species. These Cu-rich zones are encountered very rarely and if so, mostly at the surface. Figure 2D, highlighting a superposition of the Cu, Zr and O intensities, finally reveals that neither the  $Cu_{51}Zr_{14}$  compound, nor the Cu islands show any signs of oxidation. The oxygen concentration both at Cu-rich and  $Cu_{51}Zr_{14}$ -rich regions is very low and almost below the detection limit. Cu is also always found at the spots where Zr is encountered, but not vice versa.

In summary, the pre-catalyst state exhibits a quite well-defined microstructure with a clearly distinguishable chemical distribution of Cu, Zr and O species and thus, a defined  $Cu-Cu_{51}Zr_{14}$  interface.



**Figure 2:** EDX analysis of the surface and bulk region of a FIB-cut layer of the  $Cu_{51}Zr_{14}/Cu$  pre-cursor. Panel A highlights the TEM overview image, Panels B and C the individual Cu-K (green) and Zr-K (red) EDX intensity maps. Panel D shows a superposition of Cu-K, Zr-K and O-K (blue) intensities.

# 3.3. Changes to the material under MSR conditions

The as-synthesized material was subjected to *operando* DTA/TG/MS measurements to reveal the onset-temperatures of the changes under reaction conditions (Figure 3).



**Figure 3**: Two *operando* DTA/TG/MS cycles of the  $Cu_{51}Zr_{14}/Cu$  pre-cursor (top: DTA/TG, bottom: selected MS traces on a logarithmic scale). Catalytic activity starts simultaneously with the mass gain at around 473 K. In both cycles, the pre-cursor gains weight by oxidation of the Zr-content to ZrO<sub>2</sub>, which leads to a CO<sub>2</sub>-selectivity gain.

As soon as the mass gain starts in the first cycle (around 473 K), catalytic activity sets in. Up to 550 K, the CO<sub>2</sub>-selectivity is very high. Above this temperature, formation of CO starts, increases with temperature and peaks at the maximum temperature of 630 K. During the subsequent isothermal step, the CO<sub>2</sub>-selectivity increases again. As revealed by the second cycle, the loss of the CO-formation rate is irreversible. Since this behavior correlates with the mass gain (in the heating phases), it seems that the presence of  $ZrO_2$  is decisive for the CO<sub>2</sub>-selectivity. Since it is known, that elemental Cu catalysizes the reverse water gas shift reaction, the decreasing CO formation rate with decreasing temperature can be understood. The mass gain of 6.98(1) wt% (6.98 wt% expected) after two cycles of the Cu<sub>51</sub>Zr<sub>14</sub>/Cu precursor under *operando* conditions corresponds to the state of the material after catalysis, i.e. Cu/ZrO<sub>2</sub> (Figure S5).

#### 3.4. Structural state after entering the CO<sub>2</sub>-selective state

#### Structural and phase analysis by HRTEM and SAED

After an according catalytic treatment in the methanol steam refoming mixture at 623 K, the structure of the initial  $Cu_{51}Zr_{14}/Cu$  pre-cursor changes drastically. Figure 4 reveals that this affects both surface and bulk regions. The TEM image of Figure 4A now shows a rather inhomogeneous bulk structure, with interchanged zones of nanoparticle-like features with more homogeneous areas, which nevertheless show additional internal contrast. In contrast, the situation at the surface is different: here, the nanoparticles are clearly the majority species. Figure 4B and according Figures 4 B1 and 4 B2 highlight an overview image of the surface and near-surface regions, as well as close-up views of the structure directly at the surface and at the interfacial region from the nanoparticles to the more homogeneous regions. The nanoparticle structure itself exhibits a rather well-defined and narrow particle size distribution, with individual sizes of the rounded particle outlines (diameters) of about 50-100 nm.



**Figure 4:** Overview TEM images of the FIB-cut layer of the CO<sub>2</sub>-selective state of the Cu-Zr sample in methanol steam reforming. Panel A shows both the surface and bulk microstructure,

Panel B a zoom of the surface region. Insets B1 and B2 (taken from the blue boxes in the image of Panel B), show the enlarged microstructure of the Cu-rich surface area (B1) and the transition region Cu-rich - Zr-rich (B2). The homogeneous grey region at the right side in Panel B is due to Pt from the FIB process. In Panel A, the location of the surface is indicated by the white arrows.

As the structure of the catalyst entity changes that drastically, the question about the pathway of structural transformation - and in this respect to possibly identify the structural prerequisites of the active and selective site - now arises. Figure 5 highlights that this transformation during contact to the steam reforming mixture, and hence, the process of selfactivation, is in fact related to a partial oxidative decomposition of the intermetallic  $Cu_{51}Zr_{14}/Cu$  pre-cursor. As in the as-prepared state, the nanoparticle region is still mainly dominated by metallic copper species – although their amount has considerably increased in expense of the intermetallic compound. This is also directly seen in the corresponding XR diffractograms (Figure S3). Figures 5A and 5C show a TEM image of such a region and the corresponding SAED pattern (taken from the red encircled region). In short, the patterns only show peaks arising from the cubic phase of metallic Cu (space group  $Fm\overline{3}m$ , a = 3.615Å; orientation [001]).<sup>34</sup> Table 1 gives an assignment of the main reflections to the theoretical lattice spacings. In contrast (Figure 5B), the more homogeneous, slightly lamellar structure almost exclusively reveals the presence of an quite well- ordered tetragonal ZrO<sub>2</sub> phase (space group P4<sub>2</sub>/nmc, a = 3.6598Å, c = 5.152Å; orientation  $[\overline{1} \ \overline{3} \ 1]$ <sup>35</sup>. This is structurally remarkable insofar as not the thermodynamically more stable monoclinic ZrO<sub>2</sub> phase is observed. However, this perfectly fits to previous reports obtained on powder-like Cu-ZrO<sub>2</sub> catalysts, which directly correlated the high CO<sub>2</sub> selectivity in methanol steam reforming with the simultaneous existence of both copper and tetragonal ZrO<sub>2</sub>.<sup>5,6</sup> We will focus on that in more detail in the Discussion section. In Table 1, the experimentally determined positions of the reflections have been assigned to calculated lattice spacings of the tetragonal  $ZrO_2$  structure. Note that in this pattern, some spacings cannot be unequivocally assigned to either metallic Cu or tetragonal  $ZrO_2$ . Rather, some spacings fit both structures. This co-existence is plausible for two reasons: firstly, in the red circled region some nanoparticles (probably Cu) are also present. Secondly, especially the EDX analysis presented in Figure 9 reveals that indeed these regions feature both oxidized Zr and metallic Cu. Panel D corroborates this analysis, since this dark-field image not only shows pronounced contrast variations within the lamellar regions, pointing to pronounced ordering and crystallinity, but also some small bright particles, which obviously give rise to a similar azimuthal ordering in the electron diffraction patterns. (note however, here and for the analysis of the HRTEM images, that the assignment of tetragonal  $ZrO_2$  using the (101) spacing is sensitive for the presence of this particular phase, since it does not overlap with neither of the other phases (metallic Cu, Cu<sub>51</sub>Zr<sub>14</sub> or monoclinic ZrO<sub>2</sub>) being present, as determined by XRD).



**Figure 5:** Microstructural analysis of different regions of the FIB-cut layer after entering the CO<sub>2</sub>-selective state. Panels A (TEM image) and C (SAED pattern of the red circled region in Panel A) represent the Cu-rich region. Panel B highlights a corresponding Zr-rich region with

corresponding SAED pattern (taken from the red circled region in Panel B) as inset. In both SAED patterns, the radial distribution functions are shown to facilitate the analysis. Panel D shows a dark-field image of the Zr-rich region. The respective radial distribution functions have been obtained by annular integration of the respective patterns.

**Table 1:** Analysis of the SAED patterns and assignment of the experimentally determined lattice spacings to the theoretical fringes of cubic  $Cu^{34}$  and tetragonal  $ZrO_2^{35}$  as derived from analysis of the SAED patterns in Figure 5B and 5C. The left three columns represent Figure 5C, the right ones Figure 5B.

d <sub>exp</sub> /nm	d <sub>calc</sub> /nm	lattice plane	d <sub>exp</sub> /nm	d <sub>calc</sub> /nm	lattice plane
0.211	0.208	Cu(111)	0.293	0.295	t-ZrO <sub>2</sub> (101)
0.182	0.181	Cu(200)	0.211	0.210	t-ZrO <sub>2</sub> (012)/
					Cu(111)
0.128	0.128	Cu(220)	0.182	0.181	t-ZrO <sub>2</sub> (112)
					Cu(200)
0.110	0.109	Cu(311)	0.155	0.155	t-ZrO <sub>2</sub> (013)/
					Cu(220)
			0.146	0.147	t-ZrO <sub>2</sub> (202)
			0.115	0.113	t-ZrO <sub>2</sub> (114)/
					Cu(311)
			0.105	0.104	t-ZrO <sub>2</sub> (132)

The microstructural features are further worked out in detail in Figure S6, which in Panels A and B further fosters the coexistence of Zr-rich and Cu-rich regions. The Cu-rich regions exhibit almost always a similar microstructure, whereas the Zr-rich regions appear structurally more varied: more structurally homogeneous regions (Figure S6 A) are equally found as more lamellar ones (Figure S6 B). In both images, the frequently observed Moiré-fringes confirm

the previously discussed well-ordering of the individual crystallographic domains. In this respect the TEM images depicted in Figures S6 C and D show the same region, but imaged using a different tilt angle. Cu particles seem to be embedded in a structurally more homogeneous matrix (acting as a "glue" between the Cu particles), which through contrast variations upon tilting the sample also directly reveals its high crystallinity (as a guide to the eye, two identical Cu particles have been marked by white arrows in both images).

The presence of the phases after oxidative decomposition of the  $Cu_{51}Zr_{14}$  intermetallic compound in bulk and surface regions is further corroborated by dedicated high-resolution electron microscopy (Figures 6 and 7). Figure 6 thereby shows the still existing  $Cu_{51}Zr_{14}$  phase in the sample bulk, as revealed by its (202) and (311) lattice spacings ( $d_{calc}(202)=3.2$ Å;  $d_{calc}(311)=2.7$ Å; based on PDF#42-1185)<sup>36</sup>. Figure 7 highlights the atomic-scale structure of different surface and bulk regions of the material, corroborating the fact that metallic Cu is mainly found at the surface. Figure 7 A therefore reveals the (111) spacings of the cubic Cu structure ( $d_{calc}(111)=2.1$ Å). Interfacial and Zr-rich regions are shown in Figures 7 B-D, denoting the local co-existence of oxidized Zr and Cu (revealed by its (101) [ $d_{calc}(101)=2.95$ Å] and, for CuO, by its (111) spacing [ $d_{calc}(111)=2.28$ Å]) and of tetragonal ZrO<sub>2</sub> within the bulk and at the surface. ZrO<sub>2</sub> at the surface appears highly defective in places, as pronounced bending of the lattice planes by a few degrees is frequently observed.



**Figure 6:** High-resolution image of the  $Cu_{51}Zr_{14}$  intermetallic compound still being present within the catalyst bulk after entering the CO<sub>2</sub>-selective methanol steam reforming state. (202) and (310) lattice fringes corresponding to the hexagonal  $Cu_{51}Zr_{14}$  are both observed.



**Figure 7:** High-resolution electron microscopic images of different regions of the catalyst bulk and surface after entering the CO<sub>2</sub>-selective methanol steam reforming state. Panel A: metallic Cu-rich surface region; Panel B: oxidized interfacial region of Cu-tetragonal ZrO<sub>2</sub>; Panel C: oxidized Zr-rich bulk region; Panel D: oxidized Zr-rich surface region.

### Chemical composition analysis by EDX spectroscopy

So far, only mostly structural information has been provided. In order to present more global information about the chemical distribution of Cu and oxidized Zr, in Figures 8-10 the extended EDX analysis of the bulk and surface regions discussed previously only with respect to microstructure is highlighted. In all panels, for the best comparison, the respective TEM

images are also shown. Figure 8 now shows that the observed global TEM contrast can be directly linked to the associated compositional changes. The areas with bright TEM contrast are exclusively Cu-rich, whereas on the opposite, the dark regions are Zr-rich. Oxygen is also exclusively found in these regions, directly confirming that only the Zr-rich regions are selectively oxidized in the decomposition process. The EDX maps also reveal that the Zr-rich areas are in fact chemically mostly inhomogeneous with patches of Cu-richer regions intermixed. Interestingly, in some places both Cu and Zr are observed, but the oxygen intensity still appears low. Hence, these regions might be associated with the still intact  $Cu_{51}Zr_{14}$  intermetallic compound.



**Figure 8:** EDX elemental maps of the bulk region of the FIB-cut layer shown in Figure 4. Panel A: TEM image, Panels B-C: individual intensity maps of Cu-K (olive, B), O-K (green, C) and Zr-K (red, D).

In Figure 9, in combination with Table 2, a more detailed quantification of different areas is presented. This quantification has been carried out in five representative regions, indicated by the five boxes. The X-ray signal from the elemental map was integrated and the resulting spectrum was quantified. In fact, this quantification also corroborates the so far rather

qualitative discussion. Regions with a predominant amount of Cu tend to exhibit a rather low oxygen content, hence, Cu is found mainly in its metallic state (e.g. area 2). In these regions, the Zr content is also comparatively low. Vice versa, regions with a higher amount of Zr almost exclusively feature a higher amount of oxygen (e.g. area 4). In the other regions, Cu and Zr exist also in relative amounts of 1:1. These numbers should be taken only as a rough guide, since reliable quantification of the oxygen signal in EDX is difficult due to its low X-ray yield. A trend is nevertheless clearly visible.



**Figure 9:** Detailed EDX analysis of the regions shown in Figure 8. Selected relative intensities were taken from the boxes 1-5 and are jointly summarized in Table 2. Blue regions are mainly Cu-rich, red ones mainly Zr-rich. In the yellow regions, both significant Cu and Zr intensities have been found.

**Table 2:** Quantification of the EDX map of Figure 9 of the five regions indicated by the boxed areas, based on the analysis of the Cu-K, Zr-K and O-K edges.

Area	Cu at%	Zr at-%	O at-%
1	19.7	36.2	44.1

2	92.5	1.5	6.0
3	43.1	19.5	37.4
4	8.8	37.5	53.7
5	40.8	23.5	35.7

Catalytic-wise, the chemical distribution within the surface regions is most important. Hence, Figure 10 shows a detailed quantification of the surface- and surface-near regions. A coexistence of metallic Cu and oxidized Zr is clearly revealed. Two important conclusions can be drawn: firstly, the surface is clearly Cu-enriched and secondly, only Zr is exclusively oxidized. This follows from Figure 10 B, which show a superposition of Cu (olive), Zr (red) and O (blue). In these cases, the oxygen intensity is clearly highest at the spots with a corresponding high Zr intensity. The detailed EDX quantification of the boxed region in Figure 10 A reveals about  $82\pm0.1$  at.-% Cu,  $2\pm1.8$  at.-% Zr and  $10\pm0.3$  at.-% O (apart from signals of surface carbon and Pt of the FIB layer), directly showing the predominant metallic state of Cu and its massive enrichment in surface-near regions, as well as the almost exclusive oxidation of Zr. We, therefore, conclude that the surface regions are in fact a structural and chemical coexistence of metallic Cu and oxidized Zr in the tetragonal modification (cf. electron diffraction pattern Figure 5 B). These findings also very much coincide with recent investigations of the oxidative decomposition of Cu-rich Zr<sub>2</sub>Cu alloys, leading to a mixture of tetragonal and monoclinic ZrO<sub>2</sub> as well as partially oxidized Cu.<sup>37</sup>



**Figure 10:** EDX analysis of the surface regions of the CO<sub>2</sub>-selective state. Panel A: TEM image; Panel B: Superposition of O-K (blue), Zr-K (red) and Cu-K (green) intensities; Panel C: Cu-K intensity; Panel D: Zr-K intensity. EDX spectra were analyzed within the white square.

#### 3.4. Discussion and implications for catalysis

At this stage, a short discussion about the evolving structure-activity correlations should be provided. As the most crucial structural feature of the CO<sub>2</sub>-selective methanol steam reforming state, the co-existence of metallic Cu and tetragonal  $ZrO_2$  in surface and surfacenear regions has been identified<sup>31</sup>. Hence, this selective state exhibits a rather large amount of obviously catalytically beneficial Cu-ZrO<sub>2</sub> interface. This finding is in line with previous reports and assumptions of the high importance of these special interfacial regions for CO<sub>2</sub>-selective Cu-ZrO<sub>2</sub> catalysts<sup>5,6</sup>. It is worth noting, that the presence of the tetragonal modification of ZrO<sub>2</sub> is one of the key factors explaining the high CO<sub>2</sub> selectivity, although the exact role of tetragonal ZrO<sub>2</sub> – and what sets it apart from its thermodynamically more stable monoclinic counterpart in this respect - is far from being entirely clear.<sup>10-18</sup> So far, the discussion remains on a mere qualitative basis, but recently, the easy partial and reversible hydroxylation of tetragonal ZrO<sub>2</sub> has been proven by XP spectroscopy before and after entering the CO<sub>2</sub>-selective state<sup>31</sup>. Extending this argument even further, we might suggest an obviously better water activation capability of tetragonal ZrO2 compared to the monoclinic one. This water activation is an imperative prerequisite for steering the reaction intermediates resulting from the decomposition of methanol (on Cu) towards CO<sub>2</sub>. On comparable Cu-Zr inverse model systems, starting from Cu-Zr intermetallic systems or from CVD- or ALDprepared ZrO<sub>2</sub> layers and particles on Cu, the tremendous impact of the preparation routine has been worked out in detail<sup>29,30</sup>. Via these synthesis procedures it was possible to tune the structure and the hydroxylation properties of the ZrO<sub>2</sub> layers, and thus, to steer the reaction deliberately between CO, CO2 and even formaldehyde. Focussing on the impact and the possible influence of the structure of the selective Cu-ZrO<sub>2</sub> catalyst we note that an important structural parameter that is common to both metallic Cu and tetragonal ZrO<sub>2</sub> is the low lattice mismatch of the cubic Cu and the tetragonal ZrO<sub>2</sub> structure. This is evidenced in Table 1, where the observed lattice mismatch between the tetragonal  $ZrO_2$  (012) and Cu (111) planes and tetragonal ZrO<sub>2</sub> (112) and Cu (200) planes, respectively, is less than 1%. The same is true for the tetragonal ZrO<sub>2</sub> (114) and Cu (311) lattice planes, where the mismatch is smaller than 4%. This would facilitate the formation of a well-defined, extended Cu-tetragonal ZrO<sub>2</sub> interface with superior catalytic properties upon oxidative decomposition of the Cu<sub>51</sub>Zr<sub>14</sub> compound. That this structural argument is not so far-fetched is directly seen in the electron diffraction pattern of Figure 5 B, where tetragonal ZrO<sub>2</sub> appears well-ordered (note, however, that this pattern does not directly correlate to the best-match scheme presented in Figure 11, since through the FIB process, the required delicate relative alignment between sample and electron beam for perfect epitaxial visualization is not necessarily obtained). Since the initial amount of metallic Cu is very low, this suggests that during decomposition of the intermetallic compound the formation of an increased amount of metallic Cu and the oxidation of Zr to form tetragonal ZrO<sub>2</sub> takes place simultaneously, resulting in the observed epitaxial ordering. The dominating epitaxial relation hence is:

# Cu (001) || tetr. $ZrO_2(11\overline{2})$

and is schematically visualized in Figure 11. The direct epitaxial stabilization of Cu species by different Zr polymorphs has also been brought up in a recent article by Pakharukova et al., who highlighted the close epitaxial relation between CuO and monoclinic  $ZrO_2$  as (110) CuO  $\parallel$  (200)  $ZrO_2$ .<sup>38</sup> The same authors also provided evidence for the formation of epitaxial copper oxide chain-like clusters on tetragonal  $ZrO_2$ .<sup>39</sup>

We might also raise the question about the role of the structure of the hexagonal intermetallic compound  $Cu_{51}Zr_{14}$ . Certainly, some structural similarities between the structures of this compound and tetragonal  $ZrO_2$  exist (e.g. is the lattice mismatch between the (112) lattice plane of tetragonal  $ZrO_2$  and the (410) plane of  $Cu_{51}Zr_{14}$  equally pronounced; see Figure 11 C), resulting in the epitaxial relation:

$$Cu_{51}Zr_{14} (0001) \parallel tetr. ZrO_2 (11\overline{2})$$

The answer to this question would be ultimately linked to the pathway of oxidative decomposition of the intermetallic compound and to the decision at which stage exactly tetragonal  $ZrO_2$  is formed. To date, the provided microscopic images showing massive segregation and enrichment of Cu at the surface rather support the hypothesis that the formation of the well-ordered expitaxial  $ZrO_2$  layers are indeed at least in part structurally mediated both by  $Cu_{51}Zr_{14}$  and metallic Cu. These structural prerequisites, in the form of an extended Cu-tetragonal  $ZrO_2$  interface, subsequently lay the foundation for the formation of catalytically beneficial reversible hydroxylation and the formation of  $ZrO_xH_y$  species, as discussed also previously.



**Figure 11:** Ball models of the epitaxial Cu-ZrO<sub>2</sub> (tetr.) and Cu<sub>51</sub>Zr<sub>14</sub>-ZrO<sub>2</sub> (tetr.) interface. Panel A: top view of Cu (001) || tetr. ZrO<sub>2</sub> (11 $\overline{2}$ ), Panel B: side view of Cu (001) || tetr. ZrO<sub>2</sub> (11 $\overline{2}$ ), Panel C: side view of Cu<sub>51</sub>Zr<sub>14</sub> (0001) || tetr. ZrO<sub>2</sub> (11 $\overline{2}$ ) (green: Zr, red: O, blue: Cu).

#### 4. Conclusions

We have shown the microstructural evolution and requirements for obtaining a  $CO_2$ -selective state of an intermetallic Cu-Zr compound during self-activation in methanol steam reforming. Starting from a well-defined  $Cu_{51}Zr_{14}/Cu$  pre-cursor, we observe that surface, near-surface and also bulk regions of the intermetallic pre-catalyst structure are heavily influenced by the

oxidative decomposition following contact to the methanol steam reforming reaction mixture. The microstructure of the most active and CO<sub>2</sub>-selective state is characterized by a coexistence of metallic copper nanoparticles and patches of oxidized zirconium exhibiting predominantly the tetragonal ZrO<sub>2</sub> structure. This important co-existence is also found in deeper bulk regions of the sample, although generally, the catalyst exhibits a "chaotic" microstructure, with regions of homogeneous and/or lamellar patches of almost pure  $ZrO_2/Zr$ richer regions in close vicinity of embedded Cu-rich regions. An exception only concerns the surface-near regions, as discussed above. It is worth noting that this active and selective state is an exclusive result of self-activation during reaction. While this not per se a new finding, especially for the Cu-Zr system, whose importance in replacing the sintering-prone Cu-ZnO system has gained a lot of interest recently, high CO<sub>2</sub> selectivity using such a pathway has so far only be obtained by adding dopants and oxidative pre-decomposition of the intermetallic compound. In addition, in contrast to starting from glassy amorphous alloys reported earlier, the well-defined starting state allows the direct monitoring of self-activation and structural transition. Given the renewed importance of intermetallic compounds in catalysis, we anticipate that the outlined ideas might offer a convenient pathway to a generalized concept of activation of different bimetallic compounds. Further studies should also clarify, to what extent the self-activation and the oxidative decomposition is a function of the composition of the samples. So far, only one composition (starting from a mixture of Cu and  $Cu_{51}Zr_{14}$ ) has been analyzed. Given that controlling the composition in only a very narrow compositional range is imperative for activation of a number of catalytically active bimetallic compounds (such as ZnPd), more results are to be expected and likely lead to further improvement of the catalytic properties. The use of such intermetallic compounds is therefore not limited to in situ stable compounds<sup>40</sup>. Rather, access to high-performance materials, eventually not accessible by other routes, is granted<sup>41</sup>. With respect to potential application areas, we envision the formation of strongly attached self-activating catalytically selective intermetallic layer coatings on very stable supports with potential application in monolith- and microreactor techniques (e.g. bimetallic coatings of ceramic monoliths for microreactors and microreformers) which can automatically form a highly active, highly selective, and very stable high-surface-area state by "selective corrosion" under MSR reaction conditions.

# **Supporting Inormation**

Catalytic tests; X-ray diffraction patterns; additional EDX analysis; additional TEM imaging

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#### References

[1] Ali, K. A.; Abdullah, A. Z.; Mohamed, A. R.; Recent Development in Catalytic Technologies for Methanol Synthesis From Renewable Sources: A Critical Review. *Renewable Sustainable Energy Rev.* **2015**, *44*, 508-518.

[2] Behrens, M.; Armbrüster, M.; in Catalysis for Alternative Energy Generation (Eds.: L.Guczi, A. Erdôhelyi), Springer New York, 2012, pp. 175-235.

Behrens M.; Brennecke, D.; Girgsdies, F.; Kißner, S.; Trunschke, A.; Nasrudin, N.;
Zakaria, S.; Fadilah Idris, N.; Abd Hamid, S. B.; Kniep, B.; Fischer, R.; Busser, W.; Muhler,
M.; Schlögl, R. Understanding the Complexity of a Catalyst Synthesis: Co-Precipitation of
Mixed Cu,Zn,Al Hydroxycarbonate Precursors for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalysts Investigated by
Titration Experiments. *Appl. Catal. A* 2011, *392*, 93-102.

[4] Velu, S.; Suzuki, K.; Gopinath, C. S.; Yoshida, H.; Hattori, T. XPS, XANES and EXAFS Investigations of CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>/ ZrO<sub>2</sub> Mixed Oxide Catalysts. *Phys. Chem. Chem. Phys.* 2002, *4*, 1990-1999

[5] Purnama, H.; Girgsdies, F.; Ressler, T.; Schattka, J. H.; Caruso, R. A.; Schomacker,
R.; Schlögl, R. Activity and Selectivity of a Nanostructured CuO/ZrO<sub>2</sub> Catalyst in the Steam
Reforming of Methanol. *Catal. Lett.* 2004, *94*, 61-68.

[6] Purnama, H.; Ressler, T.; Jentoft, R. E.; Soerijanto, H.; Schlögl, R.; Schomäcker, R.
 CO Formation/Selectivity for Steam Reforming of Methanol with a Commercial CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. *Appl. Catal. A* 2004, *259*, 83-94.

[7] Velu, S.; Suzuki, K.; Kapoor, M. P.; Ohashi, F.; Osaki, T. Selective Production of Hydrogen for Fuel Cells via Oxidative Steam Reforming of Methanol over CuZnAl(Zr)-oxide Catalysts. *Appl. Catal. A* **2001**, *213*, 47-63

[8] Wu, G.-S.; Mao, D.-S.; Lu, G.-Z.; Cao, Y.; Fan, K.-N. The Role of the Promoters in CuBased Catalysts for Methanol Steam Reforming. *Catal. Lett.* 2009, *130*, 177-184

[9] Breen, J. P.; Ross, J. R. Methanol Reforming for Fuel-Cell Applications: Development of Zr-Containing Cu-Zn-Al Catalysts. *Catal. Today* **1999**, *51*, 521-533.

[10] Baiker, A.; Kilo, M.; Maciejewski, M.; Manzi, S.; Wokaun, A. Hydrogenation of CO<sub>2</sub> Over Copper, Silver and Gold/Zirconia Catalysts: Comparative Study of Catalyst Properties and Reaction Pathways. *Stud. Surf. Sci. Catal.* **1993**, *75*, 1257–1272.

[11] Ruh, R.; Rocket, T. J. Proposed Phase Diagram for the System ZrO<sub>2</sub> J. Am. Ceram. Soc. **1970**, *53*, 360.

[12] Koppel, R.; Stocker, C.; Baiker, A. Copper- and Silver–Zirconia Aerogels: Preparation, Structural Properties and Catalytic Behavior in Methanol Synthesis from Carbon Dioxide. *J. Catal.* **1988**, *179*, 515–527.

[13] Ma, Z.-Y.; Yang, C.; Wie, W.; Li, W.-H.; Sun, Y.-H. Catalytic Performance of Copper Supported on Zirconia Polymorphs for CO Hydrogenation. *J. Mol. Catal. A: Chem.* **2005**, *231*, 75–81.

[14] Wang, L.-C.; Liu, Q.; Chen, M.; Liu, Y.-M.; Cao, Y.; Hey-Yong; Fan, K.-N. Structural Evolution and Catalytic Properties of Nanostructured Cu/ZrO<sub>2</sub> Catalysts Prepared by Oxalate Gel-Coprecipitation Technique. *J. Phys. Chem. C* **2007**, *111*, 16549–16557.

[15] Samson, K.; Śliwa, M.; Socha, R. P.; Góra-Marek, K.; Mucha, D.; Rutkowska-Zbik, D.;
Paul J-F.; Ruggiero-Mikołajczyk, M.; Grabowski R.; Słoczyński J. Influence of ZrO<sub>2</sub>
Structure and Copper Electronic State on Activity of Cu/ZrO<sub>2</sub> Catalysts in Methanol
Synthesis from CO<sub>2</sub>. ACS Catal. 2014, 4, 3730-3741

[16] Grabowski, R.; Słoczyński, J.; Śliwa, M.; Mucha, D.; Socha, R. P.; Lachowsk, M.; Skrzypek, J. Influence of Polymorphic ZrO<sub>2</sub> Phases and the Silver Electronic State on the Activity of Ag/ZrO<sub>2</sub> Catalysts in the Hydrogenation of CO<sub>2</sub> to Methanol . *ACS Catal.* **2011**, *1*, 266–278

[17] Jung, K. T.; Bell, A. T. E€ Effects of Zirconia Phase on the Synthesis of Methanol over
 Zirconia-Supported Copper. *Catal. Lett.* 2002, 80, 63–68.

[18] Rhodes, M. D.; Bell, A. T. The Effects of Zirconia Morphology on Methanol Synthesis from CO and H<sub>2</sub> over Cu/ZrO<sub>2</sub> catalysts Part I. Steady-State Studies *J. Catal.* **2005**, *233*, 198–209.

[19] Rameshan, C.; Stadlmayr, W.; Weilach, C.; Penner, s.; Lorenz, H.; Hävecker, M.;
Blume, R.; Rocha, T.; Teschner, D.; Knop-Gericke, A.; Schlögl, R.; Memmel, R.; Zemlyanov,
D.; Rupprechter, G.; Klötzer, B. Subsurface-Controlled CO<sub>2</sub> Selectivity of PdZn Near-Surface
Alloys in H<sub>2</sub> Generation by Methanol Steam Reforming. *Angew. Chem. Int. Ed.* 2010, *49*, 3224-3227

[20] Friedrich, M.; Penner, S.; Heggen, M.; Armbrüster, M. High CO<sub>2</sub> Selectivity in Methanol Steam Reforming Through ZnPd/ZnO Teamwork *Angew. Chem. Int. Ed.* **2013**, *52*, 4389-4392

[21] Friedrich, M.; Teschner, D.; Knop-Gericke, A.; Armbrüster, M. Influence of Bulk Composition of the Intermetallic Compound ZnPd on Surface Composition and Methanol Steam Reforming Properties. *J. Catal.* **2012**, *285*, 41-47.

[22] Rameshan, C.; Stadlmayr, W.; Penner, S.; Lorenz, H.; Hävecker, M.; Blume, R.; Rocha, T.; Teschner, D.; Knop-Gericke, A.; Schlögl, R.; Memmel, R.; Zemlyanov, D.; Klötzer, B.
Hydrogen Production by Methanol Steam Reforming on Copper Boosted by Zinc-Assisted
Water Activation. *Angew. Chem.* 2012, *124*, 3057-3061.

[23] Gasser, D.; Baiker, A. Hydrogenation of Carbon Dioxide over Copper-Zirconia Catalyst
Prepared by In Situ Activation of Amorphous Copper-Zirconium Alloys. *Appl. Catal.* 1989, 48, 279-294.

[24] Domokos, L.; Katona, T.; Molnár, Á.; Lovas, A. Amorphous Alloy Catalysis VIII. A New Activation of an Amorphous  $Cu_{41}Zr_{59}$  Alloy in the Transformation of Methyl Alcohol to Methyl Formate. *Appl. Catal. A* **1996**, *142*, 151-158.

[25] Jennings, J. R.; Owen, G.; Nix, R. M.; Lambert, R. M. Methanol Synthesis Catalysts Derived from Copper Intermetallic Precursors: Transient Response to Pulses of Carbon Dioxide, Oxygen and Nitrous Oxide. *Appl. Catal. A* **1992**, *82*, 65-75

[26] Owen, G.; Hawkes, C. M.; Lloyd, D.; Jennings, J. R.; Lambert, R. M.; Nix, R. M. Methanol Synthesis Catalysts Derived from Ternary Rare Earth, Copper, Zirconium and Rare Earth, Copper, Titanium Intermetallic Alloys. *Appl. Catal.* **1990**, *58*, 69-81.

[27] Takahashi, T.; Kawabata, M.; Kai, T.; Kimura, H.; Inoue, A. Preparation of Highly Active Methaol Steam Reforming Catalysts from Glassy Cu-Zr Alloys with Small Amounts of Noble Metals. *Mater. Trans.* **2006**, *47*, 2081-2085

[28] Takahashi, T.; Inoue, M.; Kai, T. Effect of Metal Composition on Hydrogen Selectivity in Steam Reforming of Methanol Over Catalysts Prepared from Amorphous Alloys. *Appl. Catal. A* **2001**, *218*, 189-195.

[29] Mayr, L.; Klötzer, B.; Zemlyanov, D.; Penner, S. Steering of Methanol Reforming Selectivity by Zirconia–Copper Interaction. *J. Catal.* **2015**, *321*, 123-132.

[30] Mayr, L.; Shi, X.; Köpfle, N.; Klötzer, B.; Zemlyanov, D.; Penner, S. Tuning of the Copper-Zirconia Phase Boundary for Selectivity Control of Methanol Conversion. *J. Catal.* **2015**, *321*, 123-132

[31] Mayr, L.; Shi, X.; Köpfle, N.; Klötzer, B.; Schmidmair, D.; Bernardi, J.; Schwarz, S.;
Penner, S. Boosting Hydrogen Production from Methanol/Water by In Situ Activating
Bimetallic Cu-Zr, *ChemCatChem* 2016, 8, 1778-1781

[32] Zhou, S.H.; Napolitano, R.E. Phase Stability for the Cu-Zr system: First-Principles, Experiments and Solution-Based Modeling. *Acta Materialia* **2010**, *58*, 2186-2196

[33] Bsenko, L. Crystallographic Data for Intermediate Phases in the Copper-Zirconium and Copper-Hafnium systems. *J. Less-Common Met.* **1975**, *40*, 365-366.

[34] PDF#04-0836, ICDD/JCPDS Data Base, Sets 1-54, 2015

[35] PDF#50-1089, ICDD/JCPDS Data Base, Sets 1-54, 2015

[36] PDF#42-1185, ICDD/JCPDS Data Base, Sets 1-54, 2015

[37] Paljevic, M.; Tudja, M. Selective Oxidation of Zirconium in Zr<sub>2</sub>Cu, *Croatia Chim. Acta*, 1999, 72, 413-426

[38] Pakharukova, P.V.; Moroz, E. M; Zyuzin, D. A.; Ishchenko, A. V.; Dolgikh, L. Y.;
Strizhak, P.E. Structure of Copper Oxide Species Supported on Monoclinic Zirconia, *J. Phys. Chem. C* 2015, *119*, 28828-28835

[39] Pakharukova, P.V.; Moroz, E. M; Kriventsov, V.V.; Larina, T.A.; Boronin, A. I.; Dolgikh, L. Y.; Strizhak, P.E. Structure and State of Copper Oxide Species Supported on Yttria-Stabilized Zirconia, *J. Phys. Chem. C* **2009**, *113*, 21368–21375

[40] Armbrüster, M.; Schlögl, R.; Grin, Y. Intermetallic Compounds in Heterogeneous
 Catalysis – A Quickly Developing Field. *Sci. Technol. Adv. Mater.* 2014, *15*, 034803.

[41] Penner, S.; Armbrüster, M. Formation of Intermetallic Compounds by Reactive Metal–Support Interaction: A Frequently Encountered Phenomenon in Catalysis. *ChemCatChem* 2015, 7, 534-534.

# **TOC Graphic**

