Boosting Hydrogen Production from Methanol/Water by in situ activating Bimetallic Cu-Zr

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Abstract: An in situ activating bimetallic Cu/Cu₅₁Zr₁₄ pre-catalyst for hydrogen generation from methanol and water yields a very high CO₂-selectivity (>99.9 %) and a high H₂ yield. With respect to the geometric surface area of our model surface at least one order of magnitude higher TOF values were observed in comparison to supported Cu-ZrO₂ and Cu-ZnO₂-ZrO₂ reference catalysts. Evolution of structural activation monitored by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electron microscopy indicates transformation of the bimetallic Cu/Cu₅₁Zr₁₄ pre-catalyst into an active and selective state with coexistence of dispersed Cu and partially hydroxylated tetragonal ZrO₂. The outstanding performance is assigned to the presence of a high interface concentration following in situ decomposition of the intermetallic compound. These active sites result from a teamwork of Cu, responsible for methanol activation, and tetragonal ZrO₂, activating water via surface hydroxylation.

Copper-based catalysts are widely used for technical applications in methanol chemistry, with well-known examples of methanol synthesis from syngas with optimized CO/CO₂ ratio, hydrogenation/photo-reduction of CO₂ to produce “renewable” methanol, and methanol steam reforming (MSR) as the reversal of the synthesis reaction from CO₂^[1]. Controllable steering of product selectivity is an obvious key criterion for technical usage. For MSR the key targets are hence high CO₂ selectivity, low CO content and maximum H₂ yield in the reformat^[2] to realize the efficient on-board production of clean hydrogen in e.g. automotive applications. With respect to the catalytic function of ZrO₂ in methanol steam reforming, already the simple addition of ZrO₂ to the conventionally used Cu/ZnO catalysts allows for reducing the inherent drawback of purely ZnO-based catalysts,

that is, the poor sintering stability^[2]. Beneficial synergistic effects for methanol synthesis have also been described for Cu/Zn and the ternary Cu/Zn/Al system prepared by a co-precipitation technique^[3]. Synergistic Cu-ZrO₂ interactions have also been reported for Cu/ZrO₂ catalysts without ZnO, involving Cu-O-Zr bonds at the phase boundary, which are believed to play a crucial role in steering the methanol reforming reaction to maximum CO₂ selectivity^[4]. Specifically, a nanocrystalline Cu/tetragonal ZrO₂ catalyst synthesized by a polymer templating technique^[5] was reported to be more active, selective and stable in MSR than the technical Cu/ZnO/Al₂O₃ methanol synthesis catalyst^[6]. Although a beneficial effect of the redox chemistry of Cu and the Cu⁰/Cu^{oxidized} ratio at the interface is put forward as an important selectivity descriptor, alongside disorder and strain phenomena within the metallic Cu phase^[2], contradicting influence has also been reported. Both beneficial^[4a, 4b] and adverse^[4d] effects of the reducibility of Cu are found in literature. Nevertheless, any influence appears strongly connected to the quantity and quality of the, especially in situ formed, Cu-ZrO₂ interface. This is important as also the oxidic constituents of the catalyst may synergistically participate in the reaction, either by stabilizing oxygenate intermediates or by directly activating water^[2]. The latter has already been identified on Pd-ZnO^[7] and Cu-ZnO^[8] as the most important step in CO₂-selective steam reforming. Our novel approach overcomes the problems of the previously studied O₂/air oxidation of Cu-Zr amorphous glassy alloys, whose activity and selectivity had to be enhanced by the deliberate additions of noble metals (e.g. Au or Pd), further complicating the elucidation of the active and selective state^[9]. Such Cu-Zr alloys as pre-catalysts, and their subsequent activation under reaction conditions, have also been studied in CO₂ hydrogenation^[10], in partial oxidation of alcohols^[11] and in ternary systems with rare earth components for methanol synthesis^[12]. The concept of in situ oxidation of Zr⁰ under MSR conditions, reported previously^[13], is now promoted to its optimum in the present study. We exemplify the surprisingly high activity and extremely high selectivity of a bimetallic Cu/Cu₅₁Zr₁₄ pre-catalyst, in situ decomposed via contact to the MSR reaction mixture, thereby adjusting the resulting Cu-ZrO₂ interface capable of opening the proper reaction channels. Selectivity control is realized via suppression of full dehydrogenation of methanol to CO and subsequent promotion of total oxidation of intermediate oxygenates such as HCHO to CO₂ by water. With the new preparation/activation technique, the activity was scaled up to achieve a ~100 times higher CO₂ formation rate (with constant catalyst size) in comparison to ref. ^[13] and ~3 times higher than at a Cu/ZnO catalyst studied under identical conditions^[8]. An estimated turnover frequency of 18 CO₂ molecules site⁻¹ s⁻¹ was calculated by taking into account the geometric surface area of the catalyst (3.6 cm²; with an average surface atom density of 1.9x10¹⁵ Cu atoms cm⁻²). The actual surface area after the catalyst activation is very likely (significantly) higher and the calculated TOF consequently accordingly lower. TOFs reported by Breen and Ross on comparable (co-)precipitated Cu/Zr/Zn systems^[4d] are significantly lower (~0.5 H₂ molecules site⁻¹ s⁻¹).

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% of the intermetallic compound $\text{Cu}_{51}\text{Zr}_{14}$ ($\text{Ag}_{51}\text{Gd}_{14}$ type structure, space group $P6/m$, $hP68$ ^[16]). The XRD experiments clearly point out the difference to the amorphous Cu-Zr alloy precursors as documented in^[9b] (Figure 1).

Figure 1: XRD patterns of the Cu-Zr catalyst before and after in situ activation under MSR conditions. The metallic pre-catalyst state (intermetallic $\text{Cu}_{51}\text{Zr}_{14}$ and elemental Cu) changes into a mixture of Cu and oxidized/hydroxylated Zr (cf. Figure 4). Tetragonal ZrO_2 appears after contact to the MSR reaction mixture. Calculated pattern are shown as bars.

For activation, amorphous alloys are usually heated in oxygen or air for several hours. Thereafter the observed selectivity is poor and the activity low^[9b]. Instead of oxidative treatments, the Cu/ $\text{Cu}_{51}\text{Zr}_{14}$ pre-catalyst catalyst is successively activated under methanol steam reforming conditions. According to Figure 2, the maximum formation rate of CO_2 increases and the onset temperature for CO_2 formation decreases by running four identical catalytic MSR cycles (Fig. 2, panels a-d). As shown in Figures 1, 3 and 4, activation is morphologically characterized by oxidative segregation as a consequence of decomposition of the intermetallic compound $\text{Cu}_{51}\text{Zr}_{14}$ and subsequent (partial) Zr surface hydroxylation (Zr 3d BE 183.1 eV^[17]). Oxidation of the intermetallic compound thus occurs without passivating the surface with ZrO_2 . The direct comparison to the Cu/Zn system catalytically characterized in the same experimental setup^[8] reveals that the activity of the reaction-induced Cu-Zr material is much more stable and no oxidative/thermal Cu sintering was observed. Moreover, a CO_2 -formation rate of $\sim 0.9 \text{ mbar min}^{-1}$ was detected, even though the surface of the sample was less than half the size of the Cu-Zn sample^[8]. Normalized to the sample area (using identical Cu substrates), the formation rates of CO_2 and hydrogen both increased by a factor of 3 for Cu-Zr. For high purity Cu (polycrystalline 99.999 % Cu-foil) negligible formation rates of CO, CO_2 and formaldehyde are observed in our reactor setup. As expected, high purity bulk Cu is a poor (de)hydrogenation catalyst, which is likely due to its limited hydrogen desorption/adsorption properties, and is, moreover, hardly capable of water activation, being the necessary precondition for total oxidation of intermediate oxygenates toward CO_2 . For less pure Cu (99.95 %), minor formaldehyde formation rates can be detected ($1 \times 10^{-2} \text{ mbar min}^{-1}$), however, water activation is not possible and in consequence, no CO_2 is formed. A ZrO_2 layer on Zr foil is also not active for MSR^[13].

Figure 2: Methanol Steam Reforming on the initial Cu/ $\text{Cu}_{51}\text{Zr}_{14}$ catalyst. Panels a)-d) are showing four subsequent runs on the same starting material. Note that the decrease of CO_2 formation rate during the isothermal reaction is due to progressive reactant consumption (methanol conversion after 60 min $\sim 100\%$ for panel d).

According to quantitative XRD experiments, the active state is characterized by in situ oxidative decomposition of $\text{Cu}_{51}\text{Zr}_{14}$ (24(1) vol-%) in favor of the formation of elemental Cu (69(1) vol-%) and oxidized Zr: new peaks arise due to the presence of tetragonal ZrO_2 and monoclinic ZrO_2 ^[18]. The former is characterized by the relatively broad peak at a $2\theta=30.5^\circ$ (green bars in Figure 1)^[19]. Note that XPS experiments (Figure 4) also suggest a certain degree of Zr surface hydroxylation, which is plausible as water activation is extremely efficient on the catalyst and leads to both hydroxylation and an outstanding CO_2 -selectivity. In contrast to the rather homogeneous structure present in the Cu/ $\text{Cu}_{51}\text{Zr}_{14}$ pre-cursor (Figure S1-S3), contact to the MSR reaction mixture at 623 K causes catalytically beneficial restructuring of both bulk and surface regions of the bimetallic Cu/ $\text{Cu}_{51}\text{Zr}_{14}$ pre-cursor. The CO_2 -selective state is characterized by a very inhomogeneous composite structure of Cu-rich (bright in Figure 3a) and Zr-rich (dark in Figure 3a) regions. While the Cu-rich regions are still characterized by a distinct small-grain structure, the corresponding Zr-rich regions exhibit a characteristic lamellar structure, which appears locally enriched in Cu. This is also directly visible in the EDX map composed of the Cu-K and Zr-K intensities (panel b). The catalytically relevant, gas-exposed surface regions are shown in panels d)-g). Although the bright-field image (d) indicates that mostly Cu is extending to the surface, the EDX maps clearly reveal that both Cu (f) and Zr (g) are jointly found at the surface. In panel e), also the O-K intensity is shown within the overlay, directly revealing that oxygen is mostly found at the locations of Zr, indicating that the surface contains metallic Cu and oxidized Zr in coexistence. Well-ordered oxidized Zr is mostly found in its tetragonal ZrO_2 modification (panel c, diffractogram taken from the square in the

Zr-rich region indicated in panel a) and not predominantly in its thermodynamically more stable monoclinic polymorph. As a final conclusion, the most CO₂-selective state, as formed by in situ decomposition of the intermetallic compound Cu₅₁Zr₁₄ is composed of finely dispersed metallic Cu particles in coexistence with hydroxylated tetragonal ZrO₂. Additional information on the structure of the Cu-rich and Zr-rich regions, alongside further EDX mapping results, including quantification, is included in the SI, Figures S4-S8.

Figure 3: Morphology of the CO₂-selective state of the decomposed Cu/Cu₅₁Zr₁₄ pre-catalyst after contact to the MSR reaction mixture up to 623 K. a) bright-field TEM image of a FIB-cut layer perpendicular to the surface, b) corresponding EDX map of the same region using the Cu-K and Zr-K intensities, c) selected area electron diffraction of a Zr-rich region (taken from the indicated square in a)). Panels d)-g) highlight the morphology (d) and the elemental distribution (e-g) of the surface region. The surface is indicated by a white arrow. The blue and green intensities in Panels b) and e) are due to Pt from the FIB process.

Already after preparation, the formation of a ZrO₂ enriched surface region is found, formed during transport in air from the preparation setup to the analysis cluster. This layer could be removed by short Ar-sputtering (not shown). However, longer exposure to air at room temperature leads to a completely oxidized film, as evidenced by the Zr 3d peak as seen in Figure 4. With short sputtering (to remove carbon), a trend towards (inter-)metallic Zr could again be found. The hypothesis of a ZrO₂ surface layer is corroborated by the XRD patterns after synthesis. With this bulk sensitive technique, only Cu and Cu₅₁Zr₁₄ are detected before reaction. After MSR reaction cycle 1-4, the Zr 3d binding energy remains constantly at 183.1 eV. This is an additional shift of +0.7 eV with respect to the BE of bulk ZrO₂ at 182.4 eV^[20] and assigned to (partial) hydroxylation^[17]. Minor carbon formation occurs, not increasing from MSR run 1 to run 4. The O 1s binding energy remains constant. Cu oxidation could not be observed as deduced from a constant Cu 2p_{3/2} binding energy, as well as the absence of a satellite peak at 944.0 eV. The activation of the catalyst can be followed by evaluating the relative signal intensities: contrary to what expected, no fully Cu-surface blocking ZrO₂ film is formed on the surface. Instead, the Zr 3d intensity decreases and the Cu 2p signal gains intensity. In parallel, the O 1s signal decreases, corroborating the exclusive oxidation capability of Zr. This enhancement of the stability of metallic Cu directly at the surface is responsible for the progressive activation. At the same time, a high number of catalytically beneficial Cu-ZrO₂ interfacial

sites is gained by a process resembling the initial stages of selective corrosion of Cu alloys such as brass.

Figure 4: Ex situ XP spectra of the Cu/Cu₅₁Zr₁₄ pre-catalyst before and after each MSR run in the batch reactor (reaction time per run ~ 1 h) until full activation of the catalyst.

The oxidative decomposition of the intermetallic compound Cu₅₁Zr₁₄ thus leads to a composite catalytic material with unprecedented properties, which in this form has not been obtained before. The use of intermetallic compounds in catalysis is thus not restricted to in situ stable compounds to enhance the knowledge of the ongoing processes^[21], but they also can be applied to generate high-performance materials not accessible by other routes – either by decomposition or by reactive metal-support interaction^[22].

We conclude that the outstanding methanol steam reforming properties of the Cu/Cu₅₁Zr₁₄ pre-catalyst, finally characterized by an in situ formed coexistence of disperse metallic Cu and (partially) hydroxylated tetragonal ZrO₂, arise due to the effective activation of water on the latter. Simultaneously, methanol activation takes place on Cu sites, increasing in number at the surface with activation of the catalyst. Cu sites even become enhanced on the surface after the initial stages of selective corrosion of the intermetallic compound Cu₅₁Zr₁₄. The latter through in situ activation creates an active and selective Cu/tetragonal ZrO₂ interfacial coexistence at the surface. This in consequence leads to a very high number of beneficial interfacial sites bringing activated water and methanol species in the most efficient way together in close neighborhood at the same time resulting in very high activity and outstanding selectivity.

Experimental Section

To prepare 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 stacked in a Ta boat in the atomic ratio Cu:Zr = 2:1. This represents an empirical optimum ratio, although no upper limit for the Zr content in terms of forming a passivating and deactivating ZrO₂ layer covering the surface, potentially leading to a loss of Cu/ZrO₂ phase boundary was observed (see SI for Cu:Zr=9:2 and 1:2). However, practically the maximum content of Zr is limited by the completeness of the reaction between Cu and Zr. The sample holder boat is heated resistively under high vacuum conditions (base pressure $\sim 1 \times 10^{-7}$ mbar) slightly above the melting temperature of Cu (1360 K), but far below the melting temperature of Zr (2130 K). At this temperature, solid Zr reacts with the molten Cu to form a uniform melt, whereas at the same time the evaporation of Cu is negligibly low. With corresponding higher Zr content (Cu:Zr < 2:1) this reaction is not complete and solid Zr remains. In the SI (Figure S9) reactivities for samples with higher and lower initial stoichiometries (Cu:Zr=9:2 Cu:Zr=1:2) reveal no selectivity differences, but lower CO₂ formation rates compared to the optimum Cu:Zr=2:1 ratio. Cooling down to 300 K is performed within 30 min with a time-averaged cooling rate of ~ 30 K/min. At 300 K, the HV chamber is vented and the catalyst transported in air to structural and spectroscopic characterization. Optical and electron micrographs of the catalyst before and after MSR are given in the SI (Figure S10 and S11). Temperature-programmed methanol steam reforming experiments were performed using an UHV-attached high-pressure batch reactor with continuous MS detection^[14]. 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⁻¹ temperature ramp up to 623 K and an isothermal period at 623 K for 30 min.

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Keywords: methanol steam reforming • H₂-generation • water activation • Cu Zr model catalyst

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Boosting Hydrogen Production from Methanol/Water by in situ activating bimetallic Cu-Zr

Enhanced activity and stability for hydrogen generation from methanol/water by *in situ* activating Cu-Zr: An *in situ* activating Cu/Cu₅₁Zr₁₄ pre-catalyst for methanol steam reforming was prepared, showing extremely high CO₂ selectivity of >99.9% and a consequently excellent H₂ yield. The fully activated catalyst showed an enhancement of the specific activity by at least one order of magnitude compared to supported Cu-Zn catalysts due to the *in situ* formed coexistence of disperse Cu and partially hydroxylated tetragonal ZrO₂ at the surface.