Steering of methanol reforming selectivity by zirconia-copper interaction

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Abstract

“Inverse” ($\text{ZrO}_2/\text{ZrO}_x\text{H}_y$ on Cu) and “real” (Cu nanoparticles on ZrO_2) ultra-high vacuum/ambient pressure model catalyst studies were performed using methanol steam reforming as test reaction. The catalytic profile was correlated with structural and spectroscopic analysis using X-ray Photoelectron and Auger Electron Spectroscopy and High-Resolution Electron-energy Loss Spectroscopy. Access to water activation-dependent pathways is achieved by special Cu/ ZrO_xH_y phase boundary or interfacial sites formed during reaction, which were studied with respect to surface coverage, island size and chemical state of Cu/Zr metal/oxide species. On the “real” model system, particle size effects increasing the amount of unwanted CO were observed beyond interfacial selectivity-steering effects. Oxidation of Zr^0 to Zr^{+4} during reaction forms the most efficient phase boundary with respect to redox-active sites. Ability for reversible hydroxylation of Zr combined with a submonolayer Zr coverage for maximum $\text{ZrO}_x\text{H}_y/\text{Cu}$ phase boundary dimensions are the most critical parameters in catalyst preparation.

1. Introduction

Zirconia's mechanical and chemical properties make it a relevant material for several technical and industrial applications. Besides application in chemical sensors (often also in its yttrium-stabilized modification) [1-3], as protective layers, or as gate oxides in the semiconductor industries [4-6], the usage as a catalyst is currently under investigation for several systems. An excellent overview of ZrO_2 used as support as well as part of the active site in heterogeneous catalysis is given in ref. [7]. Methane combustion [8], CO_2 hydrogenation to methanol [9] and low temperature methane oxidation [10] are examples for reactions catalyzed by ZrO_2 -supported active metal particles. Recently, the attention was focused on the catalytic relevance of ZrO_2 -based cermet-materials [11] and Zr-containing alloys/intermetallic compounds for C_1 -surface reactions such as methanol steam reforming (MSR) [12] or in natural gas-operated solid oxide fuels cells [13, 14]. The latter are constructed using yttrium-stabilized zirconia as electrolyte material and therefore have enhanced thermal compatibility with catalytically active Zr-based electrodes to avoid thermal damage by different expansion coefficients. For this application numerous other materials such as Ni-based anode composites show catalytic activity and selectivity in SOFCs [15] and also progress is made regarding the coking issue and the unwanted formation of carbon-nanotubes. However, innovative Cu-based systems [16-18] have the potential for even better catalytic properties for fuel activation while suffering less from carbon-induced deactivation. In particular, with respect to MSR, meaningful Cu-Zr UHV model catalyst studies are missing so far, mostly because of the difficulties in preparing ultrathin Zr, ZrO_2 and ZrO_xH_y films using commercial preparation techniques such as thermal evaporation. This is mainly caused by disadvantageous material properties such as a high melting point in combination with low vapor pressures of both Zr^0 and ZrO_2 . Thermal evaporation of metallic zirconium has been applied by Paulidou et al. [19] based on a design using W as filament and support. To avoid

W contamination and provide atomically clean layers that are suitable for catalysis experiments we decided to use another technique. The self-developed enhanced sputter technique [20] allows us to prepare ultra clean thin films of ZrO_2 or of mixed ZrO_2/Zr species and therefore to subsequently perform model catalyst studies on $\text{Cu(ox)}/\text{Zr(ox)}$ systems relevant for C_1 -surface chemistry. The term $\text{Cu(ox)}/\text{Zr(ox)}$ is used to express the participation of both species on catalytic redox processes and describes a general oxidation state without referring to a specific one. It includes (partial) hydroxylation, (partial) oxidation, sub-oxides and all oxidation states between metallic and full oxidation (i.e. +II for Zr and +I for Cu). To better understand the >99% CO_2 selectivity described in ref. [12], the methanol steam reforming process has been selected as a model reaction. Purnama et al. synthesized ZrO_2 supported nanostructured Cu by a wet-chemical sol-gel method and subsequent reduction and found this system to be more active, more stable and more CO_2 selective than CuO/ZnO supported on Al_2O_3 [12].

As shown for the Pd-Zn [21-23] and Cu-Zn system [24], the formation of ultra-thin oxidic overlayers under reaction conditions by oxidative Zn segregation from a bi-metallic precursor leads to a maximum quantity of active sites for methanol steam reforming. This universal concept is beneficial for two reasons: A maximum of metal-oxide interface is formed due to the statistic distribution of Zn in the bi-metallic pre-catalyst, and secondly, the surface oxide layer is very thin and therefore electronically influenced by the substrate, resulting in distinct catalytic properties compared to the bulk oxide [22, 24, 25].

Hence, the aim of this study is to show the possibility to replace Zn(ox) by potentially redox active Zr(ox) species and to still form active and highly selective sites for steam reforming processes such as MSR by UHV model catalyst synthesis. Due to the outstanding thermochemical properties of zirconia (e.g. the very high melting point), a higher sintering stability of the respective “real” catalysts is likely. This might play an even more important

role when extending the studies from MSR to the SOFC-relevant methane reforming processes, meeting analogous requirements concerning water activation but needing at the same time significant higher operating temperatures (above 900 K) for efficient fuel activation.

Because of their surface sensitivity, XPS, AES, LEIS and HREELS were selected for ex-situ sample analysis and, after thorough pre-catalyst characterization, catalytic experiments were performed in our UHV-compatible recirculation batch reactor. The results clearly show the beneficial interaction between the two species Cu and ZrO_xH_y when they are present in a specific state on the surface with respect to oxidation level of Zr and surface topography.

2. Experimental Setup

UHV-chamber and batch reactor

Sample preparation and characterization was performed in an UHV chamber with attached reaction cell, described in more detail elsewhere [26]. It is pumped by a turbo molecular pump, an ion getter pump and a titanium sublimation pump resulting in a base pressure in the low 10^{-9} mbar range. For spectroscopic analysis, the chamber is equipped with a hemispherical electron and ion analyzer (Thermo Fisher Electron Alpha 110), a double anode X-ray gun (Mg/Al, XR 50, Specs) for XPS, an ion gun (Omicron 100) sufficient to produce 1 kV He^+ Ions for LEIS and an electron beam gun (KPI EGPS-2017B) for Auger electron spectroscopy. Additionally, a mass spectrometer (Balzers) for residual gas analysis, an electron beam heating unit for sample heating and an Ar^+ ion sputter gun for sample cleaning is attached. A three way gas inlet allows to dose O_2 (Messer, 5.0), H_2 (Messer 5.0) or O_2 cleaned Ar (Messer 5.0, Supelpure®-O Oxygen/Moisture trap) via leak valves into the chamber.

All XPS spectra were recorded with a Mg K α X-ray source ($h\nu = 1253.6$ eV) at 250 W and the “magic angle” to the analyzer. The rotatable sample holder allows performing manual angle-resolved depth-profiling in the range of 0° to 90°. For XPS the analyzer was operated using a constant pass energy of 20 eV. For Auger electron spectroscopy a constant electron energy of 3 keV was selected.

We evaporated Cu by a VG e⁻-beam micro evaporator using a 0.25 mm Cu wire looped around a 1 mm Ta rod as mechanical stabilizer. The evaporation rate was monitored by a water-cooled quartz crystal microbalance. Moreover, the film thickness was estimated from XPS via an attenuated overlayer model and the surface coverage via a non-attenuated model (described in detail in the supplementary information) to verify the amount of deposited material [27]. The results of these two quantification approaches are well comparable (aberrance <10%).

The Zr deposition was performed by an all self-developed and -constructed UHV-compatible mini-sputter-source that is described in detail in ref. [20]. It is mounted on a standard 2.5 in. CF flange and allows reproducible deposition of atomically clean (sub-)monolayers of either ZrO₂, when operated in O₂ (reactive) sputtering mode or Zr⁰/Zr⁺⁴O₂, with this ratio depending on the UHV and Ar sputter gas quality (amount of O containing residuals).

For catalytic testing in the ambient pressure cell, a long z-transfer rod allows fast and reliable transfer without exposure to air. The all-quartz-glass high-pressure (up to 1 bar) batch reactor is equipped with a gas chromatograph with either intermediate or continuous EID-MS detection to determine the exact gas composition at any point of reaction. Continuous partial pressure detection is performed via a capillary leak to the GC-MS. The quartz-glass reactor with a total circulation volume of 296 ml was designed to measure small reaction rates and selectivity patterns within a temperature range of room temperature up to 1300 K. A circulation pump ensures a constant flow and gas intermixing and an attached gas-premixing

unit allows to set arbitrary compositions of the attached gases (methanol, methane, deionized and degassed water, O₂, H₂ and He). The sample holder itself is entirely made of quartz glass to avoid background reactivity from hot metal parts and is designed for 20 mm x 18 mm metal foils [26].

A partial pressure of 8 mbar Argon added to all gas mixtures allows to correct for the thermal expansion due to the temperature increase and the simultaneous gas loss through the capillary for continuous MS detection. For partial pressure calculations, all base-line-corrected-MS signals were calibrated with pure substances with quantitative consideration of fragmentation. For all catalytic experiments shown in this work, the following initial conditions for MSR were applied: 12 mbar Methanol, 24 mbar water, 8 mbar Argon, He; total pressure: 1 bar. After an equilibration time of 10 min, a temperature ramp of 10 K min⁻¹ up to 623 K was set, followed by an isothermal period at 623 K. Note that due to the type of the reaction cell (batch reactor) used, only the total methanol conversion reached at the end of the isothermal reaction period for all experiments is stated. As for a discussion about mass and heat transport limitations, we refer to a thorough discussion of the catalytic setup in ref. [28].

All experiments except for the HREEL spectra were performed using a 20 mm x 18 mm foil ultra-clean Cu foil (99.9999%, Alfa Aesar) with a thickness of 0.125 mm for Cu and 0.127 mm for Zr. The foils were cleaned before loading to the UHV chamber in a water and an ethanol ultrasonic bath for 20 min, respectively.

High-resolution electron energy loss spectroscopy (HREELS)

The HREEL spectra as well as the corresponding XPS spectra were recorded in an Omicron Analysis chamber with a base pressure of 5×10^{-11} mbar on a LK HREELS 5000 spectrometer. An attached preparation chamber was used for sample cleaning and thin film sputtering. A primary electron energy of 7 eV was used. For HREELS we used a Cu(111) single crystal

because of suitable mounting on the sample holder and the better defined surface of a single crystal, resulting in higher intensity and better resolution in the HREEL spectra.

Preparation

For the “real” model system (Cu on a ZrO_2 substrate), the pristine Zr foil was oxidized in 1 bar O_2 and 623 K in the UHV-attached reactor cell to form a fully surface-covering layer of ZrO_2 (thicker than XPS analysis depth). Varying amounts of Cu were thermally evaporated on top of this ZrO_2 layer using a VG mini-evaporator. The evaporation rate was controlled by a quartz microbalance and the theoretical island height calculated from the nominal layer thickness and the Cu/ ZrO_2 surface ratio determined by LEIS.

For the “inverse” System (Zr(ox) on Cu) a Zr foil was mounted as sputter target to our self-constructed sputter source [20]. Reactive sputtering occurred already with traces of water or CO in the background sputter atmosphere (from residual gas molecules, pressure 2×10^{-9} mbar). With added O_2 fully oxidized Zr sub-monolayers on bulk Cu surfaces were produced. Figure 1 shows an angle-resolved XPS depth profile of a uniform ZrO_2 layer of 10 Å nominal thickness with a slightly pronounced shoulder towards lower binding energies indicating incomplete oxidation of Zr.

Fig. 1. Angle-resolved XPS of a sputtered 10 Å ZrO_2 layer on Cu (“inverse” model system). Surface sensitivity increases with decreasing photoelectron “take-off” angle. For experimental details see [26]. A shoulder toward lower binding energies in the $\text{Zr}3d$ region suggests a minor contribution from reduced Zr species. No major change of the oxidation state with analysis depth is observed, which indicates a constant Zr^{4+} /reduced Zr ratio within the growing layers during deposition.

This shoulder is present with similar intensity for all angles, which indicates a constant ratio of Zr^{+IV} and a more reduced Zr species within the growing layer during deposition. For ZrO_2 the Zr 3d peak position was found to be at 182.5 - 183 eV [29] and the peak position for O 1s at 530.9 eV [30]. The purified Argon (described above) was used to operate the sputter source in non-reactive sputtering mode. In addition, any other possible contaminations were minimized (i.e. by extensive degassing of all metal parts that are subject to be heated during sputtering and by removing the passivation ZrO_2 layer of the sputter target). By reducing the amount of background gas molecules, the fraction of metallic Zr could be increased up to a level of about 0.5 (Figure 9). Due to the propensity of Zr to very quickly react with oxygen and most oxygen containing molecules of the residual gas (CO , H_2O), residual Zr^{+IV} species are always present. Since both oxidation states and their interaction with Cu under MSR conditions were carefully studied, a clear correlation to catalytic results could be established. As described in detail below, the partially metallic pre-catalyst forms hydroxylated Zr under MSR conditions as determined from HREELS.

Analysis of the XPS Data

All spectra were analyzed using the CasaXPS software program, version 2.3.16 Pre-rel 1.4 (Casa Software Ltd.) [31]. A Shirley background was applied to all spectra and the associated Scofield relative sensitivity factors were considered for quantification. For peak fitting of the Zr 3d peaks a weighted sum of Gaussian and Lorentzian peak shapes (CasaXPS line shape SGL(30)) was used. A doublet separation ($\text{Zr } 3d_{5/2}$ vs. $\text{Zr } 3d_{3/2}$) of 2.4 eV for both metallic Zr [27] and zirconia [32] was used for fitting. The doublet area was kept constant at 3:2 as arising from spin-orbit d-electron coupling. Electron attenuation lengths were taken from the NIST database SR 82 [33] and the orbital asymmetric parameter from the ELETTRA online database of ref. [34]. The surface coverage was estimated by a non-attenuated overlayer model on a semi-infinite substrate for fractional coverage [35]. For thickness estimations, a

model that considers photoelectron attenuation through the substrate and the overlayer was used. While the coverage estimation is the more meaningful model for fractional (sub-) monolayers, a multi-monolayer film can be more accurately described by thickness model because of the consideration of the electron attenuation by the overlayer. For low thicknesses, the influence of the attenuation effect is low and therefore the results of both models (coverage in ML and thickness in Å) are convertible under consideration of the chemical composition of the overlayer. Details of these calculations are given in the Supplementary Information in Section A.

3. Results

3.1. “Real” model system Cu on ZrO₂

In this part of the study, we take a closer look on a zirconia substrate layer that is doped with Cu to determine the activity of new sites formed by Cu-ZrO₂ interaction. We observed a shift in selectivity as a function of Cu-overlayer thickness and particle/island shape because of the formation of special sites for fractional Cu coverages on ZrO₂. The individual product formation pattern turned out to be a function of Cu particle size, coverage and chemical state. As a direct proof for the existence of such a Cu-Zr phase boundary, ion scattering spectra for all prepared catalyst were collected (Figure 2). For the “real” system (upper panel), but also for the “inverse” system (lower panel), Cu as well as Zr can clearly be detected. Quantitative results are summarized in Table 1 as well as in Table 2.

Fig. 2. The 1 keV He^+ -ion scattering spectra on the two catalyst systems prove the coexistence of both species at the surface. The peak fit shows the deconvolution of the overlapping Cu and Zr peaks. Quantitative results for all spectra results are summed up in Table 2. The spectrum for the “inverse” model catalyst was taken on a 5.4 Å ZrO_2 -covered Cu foil (from the attenuated XPS overlayer model); the one for the “real” model catalyst sample on a 1.8 Å Cu overlayer on ZrO_2 .

Ex-situ XPS analysis

Due to the insulating ZrO_2 layer, severe charging effects up to 1.5 eV take place on the “real” model catalyst system. The most essential information about the chemical state can still be extracted, whereas the quantification is not affected at all. Since the shift caused by charging can be estimated from the Cu 2p signal because of its constant $2p_{3/2}$ binding energy of the main peak for all relevant oxidation states (Cu^0 and Cu^+ , Cu^{2+}) as well as from a correlation of the relative O 1s and Zr 3d shifts, a correction can be performed. Figure 3 highlights the BE/KE-corrected XPS spectra and X-ray stimulated-AES of the Cu LMM transition.

Fig. 3. Charging-corrected XPS and XPS–Auger spectroscopy of the Cu LMM transition before and after MSR. The appearance of a CuO-associated satellite at 944.0 eV, as well as the Auger fingerprint at kinetic energy 916 eV, indicates partial formation of Cu oxides.

The following conclusions can be drawn: (i) the oxidation state for Zr in all experiments is +IV before and after MSR reaction, (ii) no significant chemical shift in the Zr 3d region was detected, (iii) for Cu, the main state is metallic but the AES fingerprints (Figure 3 panel 4) as well as the satellite peak around 944.0 eV after MSR in the Cu 2p_{3/2} region (Figure 3, left panel) indicate the partial formation of Cu²⁺ species due to partial oxidation under reaction conditions. Therefore, not only Cu⁰ is present, but also (partially) hydroxylated Cu¹⁺ and Cu²⁺ species are likely. The corresponding Auger spectra also show a peak around 916 eV, indicating the presence of Cu⁺ species in addition to Cu⁰ [36].

Pure Cu and ZrO₂ in MSR

Figure 4 depicts the corresponding MSR experiments as formation rate vs. time curves during a heating and a subsequent isothermal period.

Fig. 4. MSR for (a) a clean 623 K annealed polycrystalline Cu foil; (b) a 1.8 Å Cu-doped oxidized Zr foil; and (c) a clean oxidized Zr foil.

As can be deduced from the low CO_2 -to- formaldehyde ratio of the reference experiment on pure ultra-clean Cu foil in Figure 4a, the latter is able to activate methanol but not to activate water molecules. The lack of active OH groups on the surface obviously disables the total oxidation pathway via adsorbed formates to CO_2 for maximum hydrogen generation. Moreover, clean copper cannot fully dehydrogenate adsorbed methanol, an anyway unwanted pathway that ends up in CO and consequently creates a catalyst poison and lowers the H_2 production. Therefore, the main product is desorbed formaldehyde with a formation rate maximum of $10 \times 10^{-3} \text{ mbar min}^{-1}$ at 580 K, as shown in Figure 4a and reported in ref. [24].

The CO₂ formation rate amounts to 3×10^{-3} mbar min⁻¹ at 550 K at maximum, while the CO formation rate is negligible over the entire experiment. Both CO₂ and formaldehyde rates drop rapidly because of deactivation by further heating up to 623 K, resulting in a total methanol conversion of around 2%. In comparison, a layer of fully oxidized pure ZrO₂ (Figure 4c) is not active for methanol activation and therefore neither MSR activity nor partial dehydrogenation to formaldehyde is possible. Formaldehyde, CO₂ and CO formation rates are close to 0 mbar min⁻¹ from 296 to 623 K and also in the isothermal reaction period at 623 K and consequently the total methanol conversion is ~0%.

Cu-doped ZrO₂ in MSR

As can be seen in Figure 4b, the selectivity pattern of pure Cu is shifted dramatically by electronic modification and/or phase boundary effects when both species are present at the surface at the same time: In general, Cu-doped ZrO₂ showed increased CO₂ activity. However, at the same time also the full dehydrogenation pathway to CO is progressively opened. This leads to a mostly unselective but considerably more active catalyst compared to pure bulk copper. Figure 4 also compares the isolated Cu and ZrO₂ catalyst components with an ultrathin Cu layer (nominal overlayer thickness 1.8 Å, Figure 4b) on ZrO₂. The main product is CO with a maximum formation rate of 25×10^{-3} mbar min⁻¹ at 560 K and the full dehydrogenation pathway toward CO is the only one that is not completely inhibited in the isothermal reaction period. Besides CO, CO₂ is also formed more efficiently, indicating partial ability for water activation/total oxidation. The CO₂ formation rate maximum is observed at a higher temperature of 610 K, and amounts to 14×10^{-3} mbar min⁻¹ which is about five times higher as compared to clean Cu. The formaldehyde desorption rate starts to rise at the same temperature as on clean Cu but reaches its maximum (15×10^{-3} mbar min⁻¹) at a slightly higher temperature of 600 K. This maximum is only slightly higher as compared to

clean Cu (factor 1.5). The total methanol conversion in this experiment is approximately 7.5%.

Varying amounts of Cu on ZrO₂ in MSR

The selectivity pattern as a function of the nominal overlayer thickness of the metallic Cu dopant is shown in Figure 5.

Fig. 5. CO, CO₂, and formaldehyde formation rates in MSR as a function of Cu overlayer thickness. This value was estimated by XPS using a model that assumes electron attenuation through the overlayer (for details see the [Supplementary Information](#)). The most pronounced rate differences appear between clean ZrO₂ and the lowest Cu coverage. With higher overlayer thickness, the selectivity pattern approaches that of clean Cu. However, some CO formation is left due to incomplete suppression of the phase boundary.

Details of the ion scattering surface ratio of Cu/ZrO₂ and the estimated mean particle height as derived from XPS, are given in Table 1.

Table 1: Overlayer thickness and particle height estimation for the “real” model catalysts

Evaporated amount Cu / Hz	LEIS ratio of Cu/ZrO ₂ on surface / %	attenuated overlayer thickness estimation for Cu via XPS / Å	Mean particle height / Å

40	24	14.7	61
10	16	1.8	11
2.5	3	0.3	10

With increasing nominal overlayer thickness and a correspondingly higher ratio Cu-to-ZrO₂, all product rates approach the one for clean Cu foil (see above). While the formaldehyde formation rate maximum rises due to an increasing number of “pure copper” active sites for methanol activation, the CO and CO₂ rates drop, as compared to the lowest Cu coverage experiment. The corresponding loss of phase boundary and, at the same time, increasing Cu particle size correlate mainly with a drop of the CO rate. Therefore, small/thin Cu particles/islands seem to play an important role in the formation of unwanted “full dehydrogenation” active sites which is clearly an undesirable effect in MSR for H₂-production. The mean particle height was calculated from the estimated overlayer thickness from XPS in correlation with the ratio of Cu on the surface from LEIS (Table 1). The results show that Cu does not cover ZrO₂, but clearly tends to form 3D clusters, as deduced from the increasing nominal particle height. Consequently, a higher amount of evaporated Cu does not necessarily lead to an increasing amount of phase boundary but rather to an increase in height of the Cu islands. Due to the island height growth, the “non-phase boundary”, purely metallic Cu area increases which is also indicated by the pure Cu-typical higher formaldehyde rate. This is particularly obvious for the highest Cu coverage sample (40 Hz, 14.7 Å Cu nominal overlayer thickness).

In summary, a modified catalytic behavior has been observed, but despite the enhanced CO₂ formation rate achieved by partially improved water activation by phase boundary sites, the prepared surface turned out to also effectively dehydrogenate methanol to CO. We refer this to an electronic size effect of small Cu particles.

3.2 “Inverse” model system ZrO_2 and ZrO_xH_y on Cu

For the “inverse” model system we prepared zirconia layers of various nominal thickness on the same polycrystalline Cu foil (99.999%) by our UHV compatible sputtering technique [20]. The Zr oxidation state was controlled by varying the reactive sputtering conditions, i.e. by controlling oxygen-containing species in the background gas (see experimental section). Hence, we prepared not only zirconia layers but also layers consisting of both zirconia and metallic Zr. These not fully oxidized Zr layers on Cu showed favorable catalytic abilities when used as a pre-catalyst for methanol steam reforming reactions by forming suitable active sites under *in-situ* conditions by *in-situ* hydroxylation (ZrO_xH_y). As for the “real” model system, ion scattering was performed to prove the co-existence of Cu and Zr on the surface (Figure 2, lower panel).

Fully oxidized Zr on Cu in MSR

In the first series of experiments, we prepared fully oxidized zirconia layers. At a fractional coverage of around 0.2 ML, as derived from the non-attenuated XPS coverage model, an estimated thickness (from the attenuated XPS estimation) of 1.3 Å was obtained. Moreover, multilayers with thicknesses up to 1.2 nm (8.8 ML) were prepared. In analogy to the experiment of Figure 3, neither pure Cu nor ZrO_2 itself shows any “full” dehydrogenation activity of methanol to CO. Interestingly, none of the “inverse” Cu- ZrO_2 and ZrO_xH_y model catalysts opened this pathway. In contrast to the Cu-nano-islands on the bulk ZrO_2 layer shown before, the “inverse” $\text{ZrO}_2/\text{ZrO}_x\text{H}_y$ phase boundary on bulk Cu does not favor the undesired full dehydrogenation reaction channel. Therefore, only the CO_2 -reaction rate and the formaldehyde rate are used to determine the performance and selectivity of the model catalysts.

As shown in Figure 6a, a much higher CO₂ selectivity could be observed on the “inverse” Cu-ZrO₂ catalyst than on the pure Cu support, where formaldehyde is always the main product.

Fig. 6. MSR for (a) a Cu foil with 8 Å ZrO₂ overlayer; (b) a Cu foil with a partially oxidized Zr overlayer (thickness: 1 Å). The formation of hydroxylated Zr species (ZrO_xH_y) occurs under reaction conditions in situ.

The shown catalytic experiments were performed on a fully oxidized ~ 1.4 Å ZrO₂-doped Cu foil. The CO₂ rate amounted up to 27×10^{-3} mbar min⁻¹, that is more than eight times the rate on clean Cu (3×10^{-3} mbar min⁻¹). In addition, the formaldehyde rate maximum is at 20×10^{-3} mbar min⁻¹ higher than on clean Cu, but only by a factor of 2. Both rate maxima are reached in the isothermal reaction period and only very low formation rates could be determined around 580 K. The total methanol conversion at the end of the isothermal reaction period is

~4%. Interestingly, very fast deactivation both of CO₂ and formaldehyde formation was observed.

Both the formaldehyde rate as well as the CO₂ formation rate increase with ZrO₂ doping whereas the CO rate is even more influenced. This makes CO₂ the main product on samples with a ZrO₂ film thickness between 1 and 8 Å. Higher coverages make the catalyst more and more behave like bulk ZrO₂ (Figure 7), most likely caused by a loss of interface and therefore a loss of bi-functionality of the catalytic surface.

Fig. 7. CO, CO₂, and formaldehyde formation rates in MSR as a function of the deposited amount of fully oxidized ZrO₂. Overlayer thickness was estimated by XPS using a model that assumes electron attenuation through the overlayer (for details see the [Supplementary Information](#)). Starting with clean Cu, the selectivity pattern changes in the fractional coverage regime and approaches the inactive state of ZrO₂ at high coverages.

Interpretation of these results suggest an important influence of ZrO₂ on the way how the individual reaction channels are steered. Since pure Cu or pure ZrO₂ are either unable to activate water and to provide weakly bound OH-groups for reaction with activated C₁-fuel or unable to activate methanol, the beneficial Cu-ZrO₂ interaction gives access to this desired reaction route (Figure 6a). This result can in principle be interpreted in terms of two phenomena; one describes the mechanism via a phase boundary phenomenon where the

availability of activated water on the surfaces suppresses formaldehyde desorption from the catalytic surface because of the competitive reaction of formaldehyde with OH-groups and a consequently opened total oxidation pathway to CO₂. A quantitative loss of phase boundary therefore results in a loss of CO₂-selectivity. With higher coverage, the ZrO₂ island area increases and, as soon as the island coalesce, the Cu-ZrO₂ phase boundary decreased again, explaining the loss of activity with nominally thicker zirconia layers. The second effect that may be speculated to play a role in the selectivity increase by Cu-ZrO₂ interaction is the potential electronic modification of ultrathin zirconia layers by the Cu support [37]. This new electronic state may enable the above-mentioned changes in activity/selectivity likely because of favorable reversible adsorption properties of the reactants. A higher ZrO₂ coverage in this case also leads to lower activity because ZrO₂ at some point gets too thick to be electronically modified by the Cu substrate.

The crucial importance of the Cu-ZrO₂ phase boundary, as compared to an exclusive “ligand” effect of Cu on the thin Zr-oxide layers, is suggested by the fact that higher coverages of ZrO₂ lead to a decrease of the formaldehyde rate. Formaldehyde is, as shown in Figure 3a (“real” model system), mostly a product stemming from the clean Cu surface. Therefore, clean Cu surface gets progressively lost with increasing ZrO₂ coverage. This effect is becoming predominant if the ZrO₂ islands get larger with respect to their Cu-covering area instead of becoming higher. If they become both larger with respect to covering area and higher, an electronic Cu-substrate influence of the thin oxide and consequently beneficial adsorption energies may combine with the extended phase boundary dimensions in a favorable manner.

The overall surface activity increases with ZrO₂ deposition. This can, to some extent, be assigned to a “sputter-effect” on the Cu surface during preparation by ZrO₂ and a consequently activated Cu surface. However, the enhanced selectivity can for sure be assigned to the beneficial Cu-ZrO₂ interaction in view of the fact that Ar⁺ sputtered Cu is

somewhat more active but still shows the same (formaldehyde selective) product pattern (see Figure S1 in the Supplementary Information).

Characterization by ex-situ XPS/AES before and after MSR

Figure 8 shows the XPS and AES spectra before and after the MSR experiments on the “inverse” Cu-ZrO₂ catalyst shown Figure 6a.

Fig. 8. XPS spectra of the fully oxidized ZrO₂ on Cu “inverse” model catalyst system before and after MSR (shown in Fig. 6a). The Cu2p_{3/2} peak is not very sensitive to the ongoing Cu⁰/Cu⁺ redox chemistry. The AES fingerprint indicates Cu⁺ and Cu²⁺ species. The peak shift of Zr3d correlates with the O1s shift and therefore suggests structural changes in the ZrO₂ overlayer (ZrO₂ particle size/shape effects).

We observed a peak shift of 0.5-0.8 eV of the Zr 3d doublet towards lower binding energies after the MSR experiments (the Zr 3d binding energy cannot be determined more precisely due to charging issues) (Figure 8, panel 2). Exactly the same peak shift is observed for the O 1s peak (Figure 8 panel 3). Therefore, this shift cannot be correlated to chemical Zr reduction but most likely can be assigned to overlayer shape effects and thus altered charging effects. It is known that small islands of an oxide species can differ in XPS binding energies from the respective bulk [35], however, charging must play a role in the insulating ZrO₂ systems too, especially if the ZrO₂ islands cluster towards 3D particle shapes. These structural changes occur at 623 K under reaction conditions (total pressures 1 bar) and can also be correlated to the catalytic results, where fast deactivation over time triggers a sharp drop of all reactions rates in the isothermal part. It is also worth mentioning, that the CO₂ formation clearly rises in

advance of the formaldehyde formation (Figure 6a). A possible explanation can be given in terms of the stability and wetting behaviour of the ZrO_2 islands: at the beginning, a thin ZrO_2 layer with the above described extended Cu/ZrO_2 phase boundary is MSR active but apparently not structurally stable. Clean Cu surface grows as a result of ZrO_2 3D cluster formation, resulting in the observed Zr 3d and O 1s peak shifts, rapid deactivation and a selectivity shift to formaldehyde (Figure 6a, 35-50 min reaction time).

The overall oxygen coverage slightly increases after MSR on all samples as derived from the XPS coverage model. This is a clear evidence for the oxidation effect of water activation. Cu^+ -Oxides that form during MSR can not be detected with XPS due to hardly distinguishable Cu^+ and Cu^0 species and the insufficient surface sensitivity of this method. With AES, a method that is more surface sensitive (a detailed description of the surface sensitivity of the used techniques can be found in ref. [26]), a change in the Cu LMM fingerprint indicates the partial formation of different oxidation states under MSR conditions (Figure 8, panel 4). Coking is not an issue since on any catalyst system of this study all carbon residues after MSR were below the XPS detection limit.

Zr^0 containing pre-catalyst

By minimizing the oxygen content of the Ar sputter atmosphere, a mixed layer consisting of metallic and oxidized Zr was prepared. The corresponding XPS Zr 3d region is shown in Figure 9.

Fig. 9. XPS Zr3d region of the mixed Zr^{+IV}/Zr⁰ overlayer on Cu before and after MSR.

In analogy to the CuZn system, oxidative segregation of metallic Zr from the pre-catalyst under reaction conditions is believed to form a maximum of phase boundary [24]. The *in-situ* oxidation is performed by water and the formed species are identified to be Zr-hydroxide species (ZrO_xH_y) as shown by related HREELS experiments (Figure 10).

Fig. 10. HREEL spectra of the mixed $\text{Zr}^{\text{IV}}/\text{Zr}^0$ overlayer (c) on a Cu(111) single crystal. Hydroxylation (b) in water leads to zirconium hydroxide ($\nu_{\text{Zr-OH}}$: 3731 cm^{-1}). (a) Annealing in vacuum and consequent loss of OH groups. Primary counts and FWHM: (a) $1.6 \times 10^5\text{ cps}/33\text{ cm}^{-1}$; (b) $9.0 \times 10^4\text{ cps}/34\text{ cm}^{-1}$; (c) $5.9 \times 10^3\text{ cps}/36\text{ cm}^{-1}$. Cu-O vibrations due to partial oxidation of the substrate during the reaction contribute in a minor way to the Zr-O vibrations around 600 cm^{-1} . A reference spectrum for Cu-O can be found in the [Supplementary Information](#).

This hydroxylation could not be seen on the previously described ZrO_2 (initially fully oxidized) zirconia catalysts. The Zr-O vibrations occur in the area between 550 and 750 cm^{-1} [38] and the second harmonics with the double wavenumber below 1500 cm^{-1} . In correlation with the XPS experiments, the freshly prepared sample contains ZrO_2 , explaining the Zr-O modes in HREELS. As soon as this sample is exposed to water ($5 \times 10^{-5}\text{ mbar}$, 623 K , 15 min), a Zr-OH vibration at about 3731 cm^{-1} [39] appears due to oxidative hydroxylation of metallic Zr. At the same time, the XPS peak assigned to Zr^0 in the Zr 3d region disappears. This provides clear evidence that the originally metallic Zr constituent is now fully oxidized/hydroxylated. These hydroxyl groups are not stable in vacuum at 623 K . Apparently because of reversible re-hydroxylation under reaction conditions, access to effective water adsorption/activation is gained and the catalytic behavior of this system is significantly different compared to the initially fully “dry” oxidized “inverse” ZrO_2 pre-catalysts (catalytic experiment in Figure 6b). Note that HREELS was performed on a Cu(111) single crystal while the catalytic experiments were performed on a polycrystalline Cu foil (compare experimental section). To ensure comparability of the experiments, analysis by XPS was performed on both samples with the same results (shown in Figure 9 for the Zr 3d region on the polycrystalline Cu foil). As the major catalytic effect, CO_2 formation starts at lower

temperature (~530 K). Formaldehyde formation is suppressed and the catalyst is more stable with respect to self-deactivation (Figure 6b). The CO₂ maximum formation rate amounts to 18×10^{-3} mbar min⁻¹ at 610 K and decreases only slightly in the isothermal reaction period. The formaldehyde formation rate maximum occurs at the same temperature, around 610 K, but is smaller (6×10^{-3} mbar min⁻¹). No CO at all was detected and the total methanol conversion is around 5%. Compared to clean Cu, the CO₂ rate is increased by a factor 6, while the formaldehyde rate is decreased by a factor of 2. The CO₂ selectivity at the rate maxima (~600 K) is higher than 75%. Optimization of the degree of hydroxylation and Zr-OH coverage have an extremely high potential to improve the selectivity pattern and are focus of further studies.

In general, strong evidence was found that hydroxylated/oxidic species of Zr are highly suitable for a promotional phase boundary interaction with Cu. An initially partially bimetallic pre-catalyst forms highly active and selective sites under realistic *in-situ* catalytic conditions.

4. Discussion

Catalytic results and estimated turn over frequencies for all prepared catalysts are summed up in Table 2.

Table 2: Summary of all reaction rates and surface analysis data that were used for estimation of turnover frequencies. Since no quantitative perimeter information is available and the activation of methanol only takes place on Cu and not on ZrO₂, TOF value estimations are based on blank Cu surface sites calculated from ion scattering data. The ratio of Cu/Zr was determined under consideration of relative sensitivity factors for LEIS by measuring the clean Cu and ZrO₂ surfaces. The overlayer thickness was calculated from XPS using an attenuated overlayer model (detail see SI).

	Over-layer thickness / Å	Cu ratio		Estimated number of surface Cu sites	Formation rate 10^{-3} / mbar min $^{-1}$			Turnover frequency based on surface Cu sites / s $^{-1}$		
		XPS	LEIS		CO $_2$	H $_2$ CO	CO	CO $_2$	H $_2$ CO	CO
Cu	-	1	1	1.35×10^{16}	3	10	-	0.03	0.09	-
Cu on ZrO $_2$ „real“	14.7	0.72	0.24	3.24×10^{15}	13	26	16	0.46	0.92	0.57
	1.8	0.23	0.16	2.16×10^{15}	14	15	25	0.75	0.80	1.33
	0.3	0.05	0.03	4.05×10^{14}	16	9	23	4.55	2.56	6.54
ZrO $_2$ on Cu „inverse“	12.3	0.23	0.12	1.62×10^{15}	3	5	-	0.21	0.36	-
	7.8	0.45	0.17	2.35×10^{15}	17	14	1	0.83	0.69	0.05
	1.4	0.90	0.64	8.61×10^{15}	27	20	3	0.35	0.26	0.04
ZrO $_x$ H $_y$ on Cu	0.8	0.95	0.80	1.07×10^{16}	18	6	-	0.19	0.06	-
ZrO $_2$	-	0	0	0	0	0	0	0	0	0

TOF values are calculated by considering all surface Cu sites as active sites. This approach was considered to be most efficient because of the fact that perimeter information of Cu/ZrO $_x$ H $_y$ islands are unavailable due to the experimental setup. The comparison of the “real” und “inverse” Cu(ox)/Zr(ox) model pre-catalysts for methanol steam reforming points out that in both cases active sites are formed under reaction conditions providing the desired bi-functionality. Therefore, this interaction is proven to be extremely relevant for fuel reforming processes. By varying the interface with respect to chemical and topological aspects, the selectivity pattern and stability of the catalysts can be beneficially shifted. The oxidation state of the Zr(ox) component turned out to be highly relevant for fuel activation and in further consequence for increasing the CO $_2$ rate. Especially in the “real” model system, where the surface zirconium was in any case fully oxidized to form a closed and uniform zirconia layer, only little improvements in the CO $_2$ rate compared to the “inverse” model catalyst studies could be achieved. The reactively sputtered ZrO $_2$ layers (fully oxidized) with a fractional coverage on polycrystalline Cu formed an already more active phase boundary. We suppose this layer to be less uniform and more defect-rich simply due to non-uniform oxidation while sputtering und structural irregularities because of the relatively high (kinetic) impact energy of sputtered ZrO $_x$. However, all Zr was found to be in the +IV state and none of these catalysts form a stable phase boundary that continuously activates water. Rather

clustering, loss of phase boundary and therefore rapid deactivation was observed. To fulfil the requirement of dynamic water activation, the oxidation state of zirconium in the pre-catalyst needs to be varied as shown in the mixed Zr^0/ZrO_2 “inverse” system. Only oxidative segregation of ZrO_xH_y under MSR conditions leads to the interface that is in the appropriate chemical state for fast and efficient reversible water splitting and is also stable under isothermal operating conditions of the catalyst. It needs to be emphasized that the involved hydroxylated oxidation state that forms the CO_2 -selective phase boundary to Cu is also a Zr^{+IV} state.

Regarding the unwanted CO formation rate a comparison of the results is also highly interesting since only the “real” system (Cu-nano islands on bulk ZrO_2) catalyzes the full dehydrogenation pathway. None of the pure constituents can do so. Therefore, this undesired pathway is most likely opened by the small Cu particles. A Cu particle/island size effect of nano-Cu itself is apparently not documented in literature, likely because such extremely small Cu particles (~ 1 nm in size) are unlikely to be studied experimentally on supported catalyst systems. Nevertheless, we may draw the conclusion that the formation of too finely dispersed Cu at least on zirconia as a support should be avoided when preparing a Cu/ ZrO_2 MSR catalyst.

Formaldehyde was formed on all Cu containing samples since formaldehyde desorption is the known main route on clean copper [24]. The formation rate is proportional to the area of clean copper. In the presence of the efficiently water activating $\text{ZrO}_x\text{H}_y/\text{Cu}$ phase boundary, the reaction channel through formates towards CO_2 is open and therefore the amount of desorbed formaldehyde is significantly decreased (factor 2).

Our studies clearly show that the control of the quality of the prepared phase boundaries it is highly relevant to steer the CO_2 -selectivity in MSR. An interface that triggers full dehydrogenation to CO and total oxidation to CO_2 , as observed for the “real” model catalyst

system, needs to be avoided, while special phase boundary $\text{ZrO}_x\text{H}_y/\text{Cu}$ sites, as present in the “inverse” catalyst, are highly beneficial for CO_2 -selectivity. The knowledge about the quality of differently prepared phase boundary types, and the control of the activation of different reaction pathways via the chosen preparation technique is an important input toward the optimization of technologically relevant real catalytic systems.

A comparison with the well-known CuZn system shows that the presented system is less active than CuZn (CO_2 formation rate around $0.6 \text{ mbar min}^{-1}$ in Ref [24]) and comparably CO_2 -selective. Rietzkopf et. al. [40] conclude from wet-chemical prepared catalysts, that Cu-Zr phase boundary has an even higher potential for CO_2 -selectivity. Compared with PdZn, a higher CO_2 rate could be achieved ($\sim 0.013 \text{ mbar min}^{-1} \text{ CO}_2$ on PdZn in Ref. [22]). While the CO_2 selectivity is pertained over the entire temperature range for the Cu-Zr system, the PdZn system shows strong CO formation above 573 K reaction temperature.

5. Conclusion

Small Cu particles/islands on a bulk ZrO_2 substrate exhibit a different selectivity pattern compared to bulk Cu and “inverse” ZrO_2 or ZrO_xH_y on Cu catalysts. The full dehydrogenation pathway that is not observed on bulk Cu is opened. Therefore, the desired CO_2 selectivity can hardly be increased in this system. The more Cu was deposited on ZrO_2 , the more it behaves like bulk Cu, exhibiting an increasing formaldehyde formation rate, a low CO_2 and an even lower CO formation rate.

Freshly sputtered, fully oxidized ZrO_2 on Cu temporarily increases the CO_2 selectivity but is not forming a stable catalyst under reaction conditions. Due to ZrO_2 clustering the formation rates (CO_2 , CO, formaldehyde) converge to zero in the isothermal reaction period.

By preparing (partially) hydroxylated ZrO_xH_y on Cu, the CO_2 selectivity becomes significantly increased. CO formation is completely suppressed and a small remaining formaldehyde rate due to the intrinsic activity of the Cu surface was detected. The MSR-promotional hydroxylation of Zr^0 was proven by HREEL spectra, clearly showing a Zr-OH vibration mode at about 3650 cm^{-1} .

Therefore, a bi-functional Cu/ ZrO_xH_y surface was identified with enhanced selectivity for fuel reforming of methanol. Quantitative optimization using other preparation techniques such as ALD to increase the ratio of hydroxylated Zr as well as tests with intermetallic Cu/Zr compounds as pre-catalysts will be in the focus of further studies.

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