Steering of methanol reforming selectivity by zirconia–copper interaction

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ABSTRACT

"Inverse" (ZrO_2/ZrO_xH_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 a 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. In 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 and submonolayer Zr coverage for maximum ZrO_xH_y/Cu phase boundary dimensions are the most critical parameters in catalyst preparation.

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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 a protective layer, or as a gate oxide in the semiconductor industries [4–6], its use as a catalyst is currently under investigation for several systems. An excellent overview of ZrO_2 used as a support as well as a 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 of reactions catalyzed by ZrO_2-supported active metal particles. Recently, 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] and in natural gas-operated solid oxide fuel cells [13,14]. The latter are constructed using yttrium-stabilized zirconia as an 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 solid-oxide fuel cells (SOFCs) [15], and

progress is also 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 ultra-high-vacuum (UHV) model catalyst studies are missing so far, mostly because of 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 ultraclean thin films of ZrO_2 or of mixed ZrO_2/Zr species and subsequently to perform model catalyst studies on Cu(ox)/Zr(ox) systems relevant to C_1 surface chemistry. The term Cu(ox)/Zr(ox) is used to express the participation of both species in catalytic redox processes and describes a general oxidation state without referring to a specific one. It includes (partial) hydroxylation, (partial) oxidation, suboxides, 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 systems [24], the formation of ultrathin oxidic overlayers from a bimetallic precursor under reaction conditions by oxidative Zn segregation leads to a maximum number 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 statistical distribution of Zn in the bimetallic precatalyst, and second, the surface oxide layer is very thin and therefore electronically influenced by the substrate, resulting in catalytic properties distinct from those of the bulk oxide [22,24,25].

Hence, the aim of this study is to show the possibility of replacing Zn(ox) with potentially redox-active Zr(ox) species and of still forming active and highly selective sites for steam reforming processes such as MSR by UHV model catalyst synthesis. Because of the outstanding thermochemical properties of zirconia (e.g., its very high melting point), a higher sintering stability of the respective "real" catalysts is likely. This might play an even more important role when the studies from MSR are extended 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 precatalyst characterization, catalytic experiments were performed in our UHV-compatible recirculation batch reactor. The results clearly show 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 the oxidation level of Zr and surface topography.

2. Experimental setup

2.1. Ultra-high-vacuum chamber and batch reactor

Sample preparation and characterization were performed in an UHV chamber with an 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 are attached. A three-way gas inlet makes it possible 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 Kα X-ray source ($h\nu$ = 1253.6 eV) at 250 W and the "magic angle" to the analyzer. The rotatable sample holder allows manual angle-resolved depth profiling in the range from 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 a mechanical stabilizer. The evaporation rate was monitored by a water-cooled quartz crystal microbalance. The film thickness was estimated

from XPS via an attenuated overlayer model and the surface coverage via a nonattenuated model (described in detail in the Supplementary Information) to verify the amount of deposited material [27]. The results of these two quantification approaches are quite 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 ZrO_2, when operated in O_2 (reactive) sputtering mode, or $Zr^0/Zr^{+4}O_2$, 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 low 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 intermixture and an attached gas-premixing unit makes it possible to set arbitrary compositions of the attached gases (methanol, methane, deionized and degassed water, O_2, H_2, 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 × 18 mm metal foils [26].

A partial pressure of 8 mbar argon added to all gas mixtures makes it possible 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 baseline-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 reaction cell (batch reactor) used, only the total methanol conversion reached at the end of the isothermal reaction period for all experiments is stated. For a discussion of 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 × 18 mm ultraclean 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 being loaded into the UHV chamber in a water and an ethanol ultrasonic bath for 20 min each.

2.2. High-resolution electron energy loss spectroscopy

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(1 1 1) 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.

2.3. Preparation

For the "real" model system (Cu on a ZrO_2 substrate), the pristine Zr foil was oxidized in 1 bar O_2 at 623 K in the UHV-attached