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**In situ NAP-XPS spectroscopy during methane dry reforming on ZrO$_2$/Pt(1 1 1) inverse model catalyst**

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**Abstract**

Due to the need of sustainable energy sources, methane dry reforming is a useful reaction for conversion of the greenhouse gases CH$_4$ and CO$_2$ to synthesis gas (CO + H$_2$). Syngas is the basis for a wide range of commodity chemicals and can be utilized for fuel production via Fischer–Tropsch synthesis. The current study focuses on spectroscopic investigations of the surface and reaction properties of a ZrO$_2$/Pt inverse model catalyst, i.e. ZrO$_2$ particles (islands) grown on a Pt(1 1 1) single crystal, with emphasis on *in situ* near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) during MDR reaction. In comparison to technological systems, model catalysts facilitate characterization of the surface (oxidation) state, surface adsorbates, and the role of the metal-support interface. Using XPS and infrared reflection absorption spectroscopy we demonstrated that under reducing conditions (UHV or CH$_4$) the ZrO$_2$ particles transformed to an ultrathin ZrO$_2$ film that started to cover (wet) the Pt surface in an SMSI-like fashion, paralleled by a decrease in surface/interface oxygen. In contrast, (more oxidizing) dry reforming conditions with a 1:1 ratio of CH$_4$ and CO$_2$ were stabilizing the ZrO$_2$ particles on the model catalyst surface (or were even reversing the strong metal support interaction (SMSI) effect), as revealed by *in situ* XPS. Carbon deposits resulting from CH$_4$ dissociation were easily removed by CO$_2$ or by switching to dry reforming conditions (673–873 K). Thus, at these temperatures the active Pt surface remained free of carbon deposits, also preserving the ZrO$_2$/Pt interface.

Keywords: inverse model catalyst, *in situ* XPS, methane dry reforming, surface structure, catalysis, IRAS, strong metal-support interaction (SMSI)

[Supplementary material for this article is available online](#) (Some figures may appear in colour only in the online journal)
As controversially discussed in the literature, the mechanism of MDR seems bi-functional. CH$_4$ is activated on the metal via dissociation [40], whereas CO$_2$ is activated on acidic/basic supports. On acidic supports, CO$_2$ is activated via formation of formates (reaction with the surface hydroxyls) and on basic supports by forming oxy-carbonates [41, 42]. For catalysts with relatively inert supports like SiO$_2$ the mechanism is considered to follow a mono-functional pathway, with only the metal activating both reactants [1, 3]. Apart from the different possible reaction pathways, the role of the metal-oxide interface has been vividly discussed [41, 43, 44].

Clearly, microscopic mechanisms of the interplay of metal and support, including potential structure changes under reaction conditions (e.g. SMSI, and the resulting loss of activity) [45, 46], need to be better understood, e.g. by utilizing a surface science approach.

Based on this motivation we have carried out a systematic surface-sensitive study of the interaction of CH$_4$/CO$_2$ with an inverse model catalyst, i.e. ZrO$_2$ particles/islands supported on a Pt(1 1 1) single crystal (also using Pt(1 1 1) as a support-free reference). Inverse model catalyst surfaces allow—when compared to powder systems—better spectroscopic identification of the surface state, metal-support interactions and the role of the interface [47]. Accordingly, the ZrO$_2$/Pt(1 1 1) model catalyst was characterized by temperature programmed desorption (TPD), infrared spectroscopy (IRAS), and x-ray photoelectron spectroscopy (XPS) (the latter also applied in situ during catalytic reaction).

2. Experimental

2.1. Laboratory measurements

The laboratory measurements (TPD and IRAS) were performed in a custom-built UHV chamber that was described elsewhere [48-50]. The preparation chamber is equipped with a differentially-pumped quadrupole mass spectrometer (MKS eVison+), LEED optics (SPECS ERLEED 1000-A), and a standard x-ray source (SPECS XR 50, with AlK$_\alpha$ and MgK$_\alpha$ anode) combined with a SPECS EA 150 PHOIBOS hemispherical analyzer. The UHV-compatible high pressure cell (‘Rupprecht design’) [50, 51] is connected to a Fourier transform IR spectrometer (Bruker Vertex 60v) and a ZnSe photoelastic modulator operating at 34kHz.

The Pt(1 1 1) single crystal (MaTek) was cleaned by sputtering with 1kV Ar$^+$ ions (p Ar = 5 x 10$^{-6}$ mbar, sputtering current = 2 µA) for 45 min followed by thermal annealing to 1070K. Crystal cleanliness was confirmed by XPS. For the inverse model system, ZrO$_2$ particles were prepared on the Pt(1 1 1) single crystal by sputter deposition of Zr (from a foil, Alfa Aesar, purity 99.5%) in 5 x 10$^{-6}$ mbar O$_2$ at RT, utilizing a custom-built sputter source for precise and reproducible deposition amounts [52]. The nominal thickness of the as-deposited ZrO$_2$ film was 0.3 nm (the thickness of a (1 1 1) oriented bulk ZrO$_2$ (O–Zr–O) layer is 0.295 nm [53]). Sputter deposition by this special technique leads to the growth of uniformly distributed ZrO$_2$ islands, as observed by scanning
tunneling microscopy (STM) [54]. Directly after deposition, the sample was annealed in \(5 \times 10^{-7} \text{ mbar} \) \(\text{O}_2\) to \(873 \text{ K}\) to fully oxidize the deposited \(\text{ZrO}_2\), to \(\text{ZrO}_2\) leading to the formation of larger \(\text{ZrO}_2\) islands on Pt(1 1 1). As shown in the following section, the coverage of the \(\text{ZrO}_2\) islands on Pt(1 1 1) was about half of a monolayer. Based on the nominally deposited 0.3 nm (monolayer), this would result in \(\text{ZrO}_2\) islands with an average thickness of two oxide layers (double layer \(\text{O}–\text{Zr}–\text{O}–\text{Zr}–\text{O}\)). All experiments (lab and synchrotron) were performed on the same sample.

Only high purity gases from Messer Austria were used for all experiments. The purity of oxygen and hydrogen was 5.0, \(\text{CO}_2\) was 4.8, \(\text{CH}_4\) was 4.5 and the purity of CO was 4.7. Additionally, in order to avoid carbonyl contaminations, a carbonyl absorber cartridge was installed in the CO gasline [49].

Experiments in the low pressure range were performed both in the UHV preparation chamber and high pressure cell. Dosing of gases was carried out using a high precision leak valve. The Langmuir coverage was calculated assuming a Dosing of gases was carried out using a high precision leak valve. The Langmuir coverage was calculated assuming a

\[ D = \frac{N}{A} \]

\(D\) being the Langmuir coverage, \(N\) the number of adsorbed atoms, and \(A\) the surface area. The pressure was monitored with a pyrometer measuring the surface temperature, as well as by a thermocouple.

### 2.2. Synchrotron measurements

The MDR \textit{in situ} experiments were conducted at two different synchrotron facilities due to different experimental requirements. The ISIS setup end station at HZB/BESSY II is capable to run \textit{in situ} experiments up to 1000 K, which is required for the MDR catalytic measurements. However, the system is not optimized for true UHV studies (i.e. the base pressure of the \textit{in situ} cell is only in the mid \(10^{-5}\) mbar range). In comparison, the SPECIES end station at the MAX IV laboratory is limited to a maximum reaction temperature of 673 K, which is below real dry reforming operational temperatures. However, the special design of this system allows true UHV investigations and (clean) \textit{in situ} experiments. This is important for the characterisation of the as-prepared state of the model catalyst and the initial exposure to the reactive gas environment. Nevertheless, benchmark experiments ensured that the experimental results of both beamlines were compatible.

#### 2.3. Bessy setup

\textit{In situ} experiments were performed at the ISIS end station of the HZB/BESSY II synchrotron in Berlin with a near-ambient pressure high energy x-ray photoelectron spectroscopy (NAP-HE-XPS) setup, which enables measurements at elevated pressures (up to 7 mbar) with photon energies ranging from \(\sim 80\) up to \(2000\) eV. The main parts are a ‘high pressure’ chamber with an attached differentially-pumped hemispherical analyser (modified SPECS Phoibos 150) including a 2D delay line detector. A detailed description of the near-ambient pressure XPS-setup is given in [56]. Samples were heated via a tantalum back sheet using an infrared laser. The temperature was monitored with a pyrometer measuring the surface temperature, as well as by a thermocouple.

#### 2.4. MAX IV setup

\textit{In situ} near ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) was performed at the high resolution XPS endstation SPECIES at the MAX IV Laboratory. The setup and beamline is described in detail in [57, 58]. Again, photon energies from \(\sim 80\) to \(2000\) eV could be chosen. The system was capable of performing ambient pressure and true UHV experiments. This is realized by using a retractable ‘high pressure cell’, which can be docked to the front aperture of the SPECS PHOIBOS 150 NAP analyser for ambient pressure experiments. During \textit{in situ} measurements only the cell was filled with gases, while the analysis chamber remained evacuated. Heating was achieved through electron bombardment of the vacuum side of the wall behind the sample seat of the high-pressure cell. With this design no hot filament was exposed to the gas environment. The sample temperature was measured with a chromel-alumel thermocouple wire pair mounted on the transferable sample holder.

Both \textit{in situ} setups are designed as continuous catalytic flow cells with gas analysis by mass spectrometry. For catalytic reactions, the interaction of the model catalysts surface with pure \(\text{CH}_4\) or \(\text{CO}_2\) was studied first (0.1 mbar in both cases). For the MDR reaction a total pressure of 0.2 mbar with 1:1 composition of \(\text{CH}_4\) and \(\text{CO}_2\) was used (during the single bunch beamtime higher pressures were not accessible). During reaction the temperature was varied stepwise from RT to \(873\) K. Reaction educts and products were followed by mass spectrometry. Additionally, a clean Pt(1 1 1) single crystal was used as reference for the MDR reaction and for peak assignments.

Surface sensitive \textit{in situ} XPS spectra were obtained with different incident photon energies (140 eV for VB, 210 eV for Pt 4f, 320 eV for Zr 3d, 420 eV for C 1s, and 670 eV for O 1s). These correspond to kinetic photoelectron energies between 130 and 150 eV, which leads to almost equal information depth (inelastic mean free path, IMFP) of \(0.5–0.6\) nm, according to NIST Standard Reference Database [59]. In case of depth profiling measurements, the photon energies were increased in multiple steps, resulting in photoelectron energies up to \(740\) eV, and an information depth (IMFP) up to \(1.5\) nm. After
3. Results

3.1. Structural characterisation by XPS, IR and TPD

Prior to the actual MDR experiments, a detailed characterisation of the as-prepared (oxidized) and annealed ZrO$_2$/Pt(1 1 1) inverse model catalyst surface was carried out to determine structure and thermal stability in UHV. Accordingly, the ZrO$_2$/Pt(1 1 1) system was heated stepwise to 673 K in UHV while measuring surface-sensitive XPS spectra at MAX IV (figure 1).

In 4.5 × 10$^{-5}$ mbar O$_2$ at 573 K a distinct Zr 3d feature could be observed at 181.7 eV (figure 1), which agrees with values reported for supported ZrO$_2$ with cluster-like structure [53, 61]. The Zr 3d signal was slightly shifted to lower binding energies (BE), presumably due to the presence of adsorbed oxygen, see the detailed discussion below (section 3.2 in situ XPS). Upon pumping off the O$_2$ background at RT and heating the model catalyst to 473 K in UHV, the main ZrO$_2$ signal shifted to 182.4 eV (expected for ZrO$_2$ islands), and an additional component appeared at 181.1 eV (figure 1). The peak shift of the main signal was likely caused by desorption of adsorbed oxygen. In line with our previous studies on supported thin ZrO$_2$ films the species at 181.1 eV can be attributed to the growth of an ultrathin ZrO$_2$ film on the Pt(1 1 1) surface (i.e. only one tri-layer of ZrO$_2$) [53] (see also the model in the discussion section). The 0.4 eV lower BE of the tri-layer in our previous study can be explained by the different substrate materials (Pt versus Pt$_3$Zr) and the different density of the cluster-related signal decreased. The formation of a PtZr alloy during annealing could not be observed, as the expected signal at 179.6 eV was absent (see figure 1) [53].

When the temperature was raised to 573 and 673 K in UHV (figure 1), the ZrO$_2$ trilayer film signal further increased (i.e. up to ~20% of the Zr 3d signal at 673 K), while the intensity of the cluster-related signal decreased. The formation of the PtZr alloy during annealing could not be observed, as the expected signal at 179.6 eV was absent (see figure 1) [53]. Also, the Pt 4f signal did not change during UHV annealing to 673 K (see supporting information figure S1 (stacks.iop.org/JPhysCM/30/264007/mmedia)). Upon reoxidation in O$_2$ atmosphere (p = 4.5 × 10$^{-5}$ mbar, 573 K, 10 min), the initial state of the surface with only ZrO$_2$ islands (on average a double-layer) was regenerated, i.e. the observed spreading of ZrO$_2$ on Pt(1 1 1) was reversible.

To learn more about the structure of the ZrO$_2$/Pt(1 1 1) inverse model catalyst, infrared measurements were performed, using CO as probe molecule (figure 2(a)). After exposure of the (oxidized) inverse model catalyst surface to 4 L CO at RT, a distinct feature at 2090 cm$^{-1}$ was observed, characteristic of on-top CO adsorbed on the uncovered Pt(1 1 1) surface [64] (CO does not adsorb on the ZrO$_2$ surface at these conditions [53]). To quantify the amount of adsorbed CO, TPD spectra were acquired after 4 L CO were dosed to the sample surface at 300 K (figure 2(b)). A desorption feature with a peak maximum at ~390 K originating from Pt(1 1 1) was observed [65].
(corresponding to a desorption energy of ~98 kJ mol\(^{-1}\)). By comparison with the area of desorption from the clean Pt(1 1 1) surface (with a CO saturation coverage of 0.5 ML at 300 K), it can be estimated that ~50% of the Pt surface was covered by the ZrO\(_2\) nanoparticles/islands. Accordingly, these islands must be ~0.6 nm in thickness but their average size is currently unknown (note that Lackner et al reported the growth of small islands (about 2–5 nm in size) when depositing ZrO\(_2\) by the same method on a Rh(1 1 1) single crystal [54]).

Upon annealing ZrO\(_2\)/Pt(1 1 1) in UHV to 423 K (figure 2(a)) and re-dosing 4 L CO at RT, the amount of adsorbed CO was reduced and shifted to lower wavenumber (~2080 cm\(^{-1}\)). This is in line with XPS spectra (figure 1), indicating the onset of formation of an ultrathin ZrO\(_2\) film covering more and more of the Pt(1 1 1) surface. After this series of IR spectra, the model catalyst surface was reoxidised and again exposed to 4 L CO at RT (figure 2(a), top spectrum). The obtained infrared signal was comparable to the initial signal after model catalyst preparation, with a peak at 2090 cm\(^{-1}\) of similar signal intensity. The XPS and infrared data point to the conclusion that upon UHV annealing (reduction) the ZrO\(_2\) islands started to wet the Pt surface, whereas exposure of the inverse model catalyst to oxidising conditions re-established the ZrO\(_2\) islands/clusters and the initial amount of uncovered Pt(1 1 1). This is an important finding, because it is essential to know whether under dry reforming reaction conditions the ZrO\(_2\) islands may wet/cover the Pt(1 1 1) surface, causing a pronounced surface modification of the catalyst (that may be beneficial or detrimental for the catalytic performance).

### 3.2. In situ NAP XPS studies

Before the actual MDR experiments, the interaction of the inverse model catalyst surface with the individual reactants (i.e. with CH\(_4\) or CO\(_2\) separately) was tested. This provides useful information on the reactivity of the respective molecule on the surface and its temperature-dependent effect on the surface structure/composition.

#### 3.2.1. CH\(_4\) exposure to ZrO\(_2\)/Pt(1 1 1)

Figure 3 summarises the in situ XPS results for exposure to 0.1 mbar CH\(_4\) at increasing temperature (measured at BESSY II).

For the pristine model catalyst surface (regenerated at 673 K in 4.5 × 10\(^{-5}\) mbar O\(_2\)) the binding energies are 181.7 eV for Zr 3d, corresponding to the ZrO\(_2\) particles/islands, and 71 eV for Pt 4f of the Pt(1 1 1) substrate (metallic Pt) [69]. No carbon traces were observed on the surface. Upon dosing of 0.1 mbar CH\(_4\) at 673 K the signal of the ZrO\(_2\) clusters shifted to 182.3 eV. A similar shift was observed in the O 1s signal, whereas the Pt 4f signal stayed at 71 eV.

To explain the binding energy shift of the Zr 3d and O 1s signals a closer look on the O 1s peak components is needed (note that the peak fitting for O 1s is strongly simplified as multiple factors have to be considered, see the supporting information for a detailed discussion). Upon oxidative treatment two components could be observed: a low BE component at ~529.2 eV (blue, figure 3) whose intensity turned out to be rather unaffected by the atmosphere (pointing to a ‘island-bulk like’ ZrO\(_2\)), and a high BE component at ~530.1 eV (green), whose intensity depended on the atmosphere (pointing to surface or interface oxygen species that can be removed or replenished; e.g. O from ZrO\(_2\) at the interface with possible charge transfer from O to Pt support [70, 71]).

Upon switching from O\(_2\) to CH\(_4\) atmosphere, which produces C and H on the free Pt surface, the surface/interface oxygen vanished, leading to a decrease in intensity of the high BE (530.7 eV, green) component.
Note that at the same time the entire O 1s and Zr 3d signals shifted to higher BE. With increasing temperature, the Zr 3d signal shifted even more whereas O 1s did not. When comparing the O 1s spectra of the experiments described below (pure CO2, switching from CH4 to CO2 and dry reforming with CO2/CH4) a clear trend can be identified. For oxygen-rich/oxidizing conditions an increased intensity of the high BE component (green) can be found and additionally a total shift of Zr 3d and O 1s to lower BE is observed. In contrast, for reducing conditions (UHV, CH4) the intensity of the high BE component of O 1s was much lower and peaks of O, Zr were located at higher BE. For the initial state of the (oxidized) model catalyst surface or for more oxidizing reaction conditions, we can thus propose that the higher abundance of surface/interface oxygen lead to a relative downshift of the O 1s and Zr 3d signals. For reducing conditions (UHV, CH4), less surface/interface oxygen is present and thus the Zr 3d and O 1s signals are located at the expected values. Following this discussion, Norton et al reported that the surface work function depends on the coverage of adsorbate molecules, as shown for CO adsorption on Pt(1 1 1) [72].

In the C 1s spectra the formation of graphitic carbon (283.9 eV) was observed at 673 K. Also, trace amounts of carboxylic/carboxylic species (286 eV) were present with a corresponding component in the O 1s spectra at 531.8 eV. These carbon species result from the dehydrogenation of CH4 on Pt [73] and reaction of C/CHx species with surface oxygen. Similarly, Fuhrmann et al showed that upon CH4 adsorption and dehydrogenation on Pt(1 1 1) above 550 K the dominant species formed was graphitic carbon [74]. For the oxidized surface (673 K, p(O2) = 4.5 × 10−5 mbar) trace amounts of PtOx (74.3 eV) were also observed in the Pt 4f spectra, which vanished upon CH4 exposure.

Upon raising the temperature to 773 K, the amount of graphitic carbon on the surface increased, as more CH4 was dehydrogenated to carbon. In the Zr 3d signal, a small shift to 182.4 eV was observed, whereas the Pt 4f and O 1s spectra did not change significantly. At the highest temperature (873 K) the amount of surface carbon drastically increased. Also, the Zr 3d signal showed some major changes. Again, the signal of the ZrO2 clusters shifted further to higher BE (182.5 eV), and the evolution of a new small signal at 181 eV was observed.

Figure 3. In situ XPS spectra of the ZrO2/Pt(1 1 1) inverse model catalyst during 0.1 mbar CH4 exposure at increasing reaction temperature. The bottom spectra were recorded prior to CH4 exposure in p(O2) = 4.5 × 10−5 mbar at 673 K.
As already described in the previous section, this results from the formation of small patches of a ZrO$_2$ trilayer film on the surface [53]. Again, the Pt 4f signal did not change, excluding the formation of a PtZr alloy or other changes of the substrate material (see supporting information for further discussion on the limits of spectral resolution for Pt 4f). When switching back to oxidative conditions (673 K in 4.5 x 10$^{-5}$ mbar O$_2$), as before CH$_4$ exposure, the signals of Zr 3d and O 1s shifted back to their initial state and all carbon was removed from the surface.

3.2.2. CO$_2$ exposure to ZrO$_2$/Pt(1 1 1). In the next step, the interaction of CO$_2$ with the ZrO$_2$/Pt(1 1 1) model catalyst surface was studied by introducing 0.1 mbar CO$_2$ into the in situ cell at 673 K, followed by increasing the temperature step-wise to 873 K while measuring in situ XPS spectra. Similar to the CH$_4$ experiment, the position of the Zr 3d signal before CO$_2$ exposure was at 181.8 eV. However, the CO$_2$ atmosphere caused no significant change of the Zr 3d peak position and composition for all temperatures (673, 773 and 873 K, see supporting information figure S2). Compared to exposure to pure CH$_4$, the formation of a ZrO$_2$ trilayer film at 873 K was not observed, indicating that CO$_2$ stabilized the cluster structure (i.e. the gas atmosphere has a rather oxidizing potential, which maintains the particle structure). Additionally, no significant changes were observed for C 1s, O 1s and Pt 4f. No carbon formation occurred at all temperatures and the Pt 4f signal was constant at 71 eV. The peak maxima of O1s stayed between 529.6 and 529.8 eV without major changes of the peak shape. This leads to the conclusion that CO$_2$ did not alter the model catalyst surface (and did not remove surface/interfacial oxygen), but it seems to have a stabilizing effect on the ZrO$_2$ particles (see also the model in figure 6). As shown in the previous section (figure 1), in UHV the formation of the ZrO$_2$ ultrathin film was observed already at 473 K.

3.2.3. CH$_4$ + CO$_2$ switching on ZrO$_2$/Pt(1 1 1). Following the studies of the interaction with the individual reactants, we have examined the effect of switching from 0.1 mbar CH$_4$ (mainly leading to carbon formation on the surface) to
0.1 mbar of CO₂. As shown in figure 4, the entire C 1s signal immediately vanished after switching from CH₄ to CO₂ atmosphere at 673 K.

The pathway for surface carbon removal under these conditions is via the Boudouard-reaction (C + CO₂ → 2CO) with CO₂ reacting with the surface carbon [75]. For MDR on noble metal catalysts, Qin et al also reported the efficient removal of surface carbon via this pathway for Rh, Ru, Ir, Pd and Pt supported on MgO [76].

When changing from (reducing) CH₄ to CO₂ the Zr 3d signal shifted from 182.4 to 181.7 eV and the O 1s spectra shifted from 530.3 (531.6) to 529.5 (530.7) eV. Apparently, CO₂ has an oxidizing effect (CO₂ → CO + O), most likely via CO₂ activation at the ZrO₂/Pt interface and/or the (reduced) ZrO₂ islands. This leads to re-oxidation of the reduced surface/interface sites, as deduced from the strong intensity increase of the O1s component at higher BE (green) upon changing from reducing (CH₄) to more oxidizing conditions (CO₂). This is attributed to the changing gas phase and the resulting surface work function change of the ZrO₂ particles, as discussed above. The Pt 4f signal was not affected with a constant peak position at 71 eV.

Reference measurements on pure Pt(1 1 1) (see supporting information S3) showed that the removal of surface carbon by CO₂ also occurs in the absence of the ZrO₂ particles/islands, indicating that Pt is catalysing the carbon removal by CO₂. Unfortunately, the amount of surface carbon was too low to obtain meaningful catalytic data (by CO mass spectrometer detection) to clarify whether the ZrO₂ support has an additional promoting effect on CO₂ activation and on carbon removal.

3.2.4. CH₄ + CO₂ mixture on ZrO₂/Pt(1 1 1). After static and switching studies of the individual reactants, the actual MDR reaction was examined in situ. Following the usual oxidative treatment of the ZrO₂/Pt(1 1 1) inverse model catalyst (673 K, p(O₂) = 4.7 × 10⁻⁵ mbar), a total pressure of 0.2 mbar of CH₄ and CO₂ (1:1 ratio) was introduced into the HP cell at 673 K (figure 5).

Upon exposing the surface to the reactive gas atmosphere, the Zr 3d signal shifted from 181.7 to 181.9 eV.
small shift was observed in the O 1s spectra (529.3/530.3–529.6/530.6 eV). As discussed earlier, the reason for the peak shifts of Zr 3d and O 1s is a removal of surface/interface oxygen species from the ZrO₂ particle/island surface. For the dry reforming reaction the peak shift—and the intensity change of the ‘dynamic’ high BE O 1s compound (green)—is not as pronounced as for pure CH₄ because a 1:1 mixture of CH₄ and CO₂ was used. The gas atmosphere has therefore less reducing potential due to oxygen supply by CO₂. Prior and during exposure to CH₄ + CO₂ mixture, no carbon signal was observed in the C 1s spectra, and the Pt 4f signal remained at 71 eV. When increasing the reaction temperature to 773 and 873 K no further changes appeared in the Zr 3d, C 1s and Pt 4f spectra. Only the high binding energy component of the O 1s signal slightly shifted by 0.1 eV to 530.6 eV. These observations indicate that the ZrO₂ particles were stable during reaction up to 873 K. There was no formation of a ZrO₂ ultrathin film wetting the Pt surface and thus no change in the amount of (reactive) sites. This shows that, at least under the applied conditions, no strong metal-support interaction (in the form of oxide wetting) occurred. Also, the surface stayed free of carbon deposits that would reduce the catalytic performance (a well-know effect especially for Ni catalysts). At lower reaction temperature (below ~500 K) carbon formation was observed. When the reaction temperature was raised from 773 to 873 K, mass spectroscopy detected minimal levels of CO/H₂ (not shown) but the active surface area of the inverse model catalyst (~1 cm²) was too small for meaningful acquisition of catalytic data in the BESSY II Setup.

4. Discussion

The current UHV and in situ NAP-XPS studies of an inverse model catalyst of ZrO₂ nanoislands on Pt(1 1 1) have shown that reducing conditions (UHV or CH₄) lead to the formation of an ultrathin ZrO₂ trilayer film partially covering the active Pt(1 1 1) surface. A schematic of the observed processes is presented in figure 6.

This relates our study to technological applications, as SMSI upon reduction in hydrogen can lead to an increase or loss of catalytic activity, depending on reduction temperature [45, 46, 77]. A rational explanation is that at increasing reduction temperatures the noble metals are successively covered due to the overgrowth of thin oxide layers (often considered as sub-oxides originating from the support) [78–81]. In the initial stages, this may create additional active metal-oxide interfaces [82] but with successive encapsulation the metal may be fully blocked [83, 84]. Along these lines, Stagg-Williams et al demonstrated that Pt/ZrO₂ catalysts reduced at 473 K showed higher activity for MDR than the catalyst reduced at 773 K [85]. Similarly, Faroldi et al highlighted for dry reforming on Ru/La₂O₃–SiO₂ that reduction at 673 K induced higher activity than reduction at 823 K of the same catalyst [86]. Thus, for activation of noble metal catalysts, oxidation is typically followed by low temperature reduction.

Interestingly, also in the case of our inverse model catalyst, reducing conditions (UHV or CH₄) initiated SMSI, whereas (pure) CO₂ and the reaction environment (CO₂/CH₄ 1:1 mixture) had a stabilizing effect on the ZrO₂ particle structure (and surface/interface oxygen), preventing the formation of a wetting ultrathin ZrO₂ film, thus preserving the active Pt surface area. Furthermore, during MDR at 673–873 K the surface remained free of any carbon deposits due to efficient carbon removal by CO₂ via the Boudouard reaction.

5. Conclusions

An inverse model catalyst of ZrO₂ clusters/islands supported on Pt(1 1 1) has been characterized after oxidation, when exposed to the individual reactants (CH₄ or CO₂) and in situ during the MDR reaction up to 873 K. The XPS data indicated that the ZrO₂ particles were reversibly wetting the Pt surface.
upon annealing (reduction) in UHV or under reducing (CH₄) conditions, via the formation of an ultrathin ZrO₂ trilayer film. Upon reoxidation in O₂ the initial ZrO₂ particle structure and surface/interface oxygen were reestablished. Infrared spectroscopy of the probe molecule CO adsorbed on Pt(1 1 1) was used for confirmation, as the on-top CO signal reversibly diminished and reappeared upon UHV annealing and reoxidation, respectively. Exposure to pure CH₄ at reaction temperatures led to the formation of carbon deposits. By switching to pure CO₂ the surface carbon was easily removed via the Boudouard reaction. For the actual MDR reaction (CH₄/CO₂ 1:1) the ZrO₂/Pt(1 1 1) inverse model catalyst was stable from 673 to 873 K. The Pt surface remained free of carbon and ZrO₂ remained in its oxidized state and island structure. In comparison to reducing UHV and pure CH₄ atmosphere, for which the formation of a wetting ZrO₂ trilayer film was observed, the dry reforming reaction environment was stabilizing the catalyst surface structure, preventing any SMSI effect to occur.

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