

Microscopic Insights into Methane Activation and Related Processes on Pt/Ceria Model Catalysts**

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Ceria-based supported noble-metal catalysts release oxygen, which may help to reduce the formation of carbonaceous residues, for example during hydrocarbon reforming. To gain insight into the microscopic origins of these effects, a model study is performed under ultrahigh-vacuum conditions using single-crystal-based supported model catalysts. The model systems are based on ordered CeO₂(111) films on Cu(111), on which Pt nanoparticles are grown by physical vapor deposition. The growth and structure of the surfaces are characterized by means of scanning tunneling microscopy, and the electronic structure and reactivity are probed by X-ray photoelectron spectroscopy. Specifically, it is shown that the fully oxidized CeO₂ thin films undergo slight reduction upon Pt deposition (CeO_{1.99}). This effect is enhanced upon annealing (CeO_{1.96}),

thus indicating facile oxygen release and reverse spillover. The model system is structurally stable up to temperatures exceeding 700 K. The activation of methane is investigated using high-kinetic-energy CH₄ (0.83 eV), generated by a supersonic molecular beam. It is shown that dehydrogenation occurs under rapid formation of CH or C species without detectable amounts of CH₃ being formed, even at low temperatures (100 K). The released hydrogen spills over to the CeO₂ support, which leads to the formation of OH groups. At 200 K and above, the OH groups start to decompose leaving additional Ce³⁺ centers behind (CeO_{1.97–1.94}). At up to 700 K, carbon deposits are quantitatively removed by reaction with oxygen, which is supplied by reverse spillover from the CeO₂ film, thus leading to substantial reduction of the support (~CeO_{1.90–1.85}).

1. Introduction

The limited resources of crude oil have stimulated an extensive search for new sources of energy and, in particular, fuel.^[1] Here, the activation of methane, which may originate from both natural gas fields and biogas, holds a large potential. Methane may be converted to liquid fuels by reforming (conventional or dry reforming using CO₂) and Fischer–Tropsch synthesis or, potentially, even via oxidative coupling of CH₄. One of the key problems for dry reforming catalysts is their rapid deactivation.^[1–6] For supported noble-metal catalysts, catalyst poisoning occurs due to accumulation of carbonaceous deposits on the active surface sites of the noble metals. These carbonaceous residues are basically immobile and, for example, methyl or ethylidyne on Pt may further decompose to carbidic species.^[7–9] Previous studies have shown that carbidic carbon may agglomerate to form small particles at elevated temperature,^[7,10] which may further be transformed into highly inert graphite.^[11,12]

Accordingly, one concept to avoid carbon poisoning would involve the oxidative removal of carbonaceous species before the aggregation and formation of graphitic carbon can occur. Towards this aim, the use of reducible oxides such as cerium dioxide (CeO₂) may provide a key concept.^[5,6,13] Facile oxygen release may give rise to a self-cleaning functionality, if oxygen release is rapid in comparison to the aggregation of carbon. The use of ceria in many catalytic applications involving dynamic oxygen uptake and release is well established.^[13–16] This includes, for example, its application as an oxygen-storage compound (OSC) in automotive exhaust catalysis or as a water

gas shift (WGS) catalyst to remove CO during the generation of high-grade hydrogen streams.^[13–18]

In spite of the clear involvement of CeO₂ in the reaction via a Mars–van Krevelen mechanism (see, e.g., refs. [19,20]), numerous mechanistic details of the actual reaction pathways are not yet understood. For ceria-supported noble-metal catalysts, the enhanced activity with respect to the WGS reaction was, for example, explained by charge transfer from the supported metal particles^[21,22] and Au^{δ+} and Pt^{δ+} centers formed at the boundaries between the particles and the oxide support. Recently, Matolín and co-workers have directly observed the formation of Ce³⁺ centers on stoichiometric CeO₂ films on Cu(111) upon deposition of Au and Pt by resonance photoelectron spectroscopy (RPES).^[23,24] Other concepts favor reverse spillover of lattice oxygen to the surface of the supported metal nanoparticles. Zhdanov and Kasemo^[25] argued, for example, that the energy of an oxygen atom on a Pt nanoparticle is similar to that for an ion in the surface layer of the CeO₂, with

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[**] Formation of Carbonaceous Residues, Hydrogen and Oxygen Spillover, and Self-Cleaning

the activation barrier for reverse spillover via the particle boundary being rather low. Experimental evidence for reverse oxygen spillover has been obtained by oxygen isotopic exchange studies on Rh/CeO₂.^[26,27] Additional evidence was obtained from temperature-programmed desorption (TPD) studies, for example, by Zafiris and Gorte on the same system, which suggested that lattice oxygen migration to the Rh particles occurs at about 400 K.^[28] Finally, some additional evidence for the oxygen reverse spillover from CeO₂ to Pd was obtained by Smirnov and Graham.^[29] The authors observed the oxidation of supported Pd particles while annealing the sample in ultrahigh vacuum (UHV) at temperatures above 473 K.

Herein, we used a single-crystal-based model catalyst to investigate the individual steps of carbon deposition, spillover, and removal in detail. The catalyst is based on an ordered CeO₂(111) film, prepared on Cu(111) according to a procedure recently described by Matolín and co-workers.^[30,31] The model catalyst is prepared by physical vapor deposition (PVD) of Pt on this CeO₂(111)/Cu(111) substrate under well-controlled conditions in UHV. It is accessible for most surface science experimental methods including scanning tunneling microscopy (STM) and photoelectron spectroscopies. The interaction of CH₄ with the Pt/CeO₂(111)/Cu(111) model catalyst is probed using high-kinetic-energy CH₄ generated from a supersonic molecular-beam source. This procedure is required for studies on methane activation under UHV conditions due to the very low sticking coefficient at thermal energies.^[8,9] Although CH₄ activation on noble-metal single crystals has been studied in great detail by numerous groups, very few studies have yet been performed on supported metal particles (see, e.g., ref. [32]). Herein we aim to identify the individual steps of methane activation, dehydrogenation, and oxidation. A special focus is the critical role of spillover and reverse spillover processes, which lead to the reduction of the oxide support and to self-cleaning of the model system from carbonaceous residues.

2. Results and Discussion

2.1. Morphology and Thermal Behavior of Pt/CeO₂/Cu(111)

First, we investigated the morphology and thermal stability of the Pt/CeO₂/Cu(111) model catalyst by means of STM and X-ray photoelectron spectroscopy (XPS). Towards this aim, ordered CeO₂(111)/Cu(111) films were prepared according to the procedure suggested by Matolín et al.^[30,31] Pt nanoparticles were deposited on this support at 300 K under UHV conditions.

Selected STM images obtained at different stages of preparation and thermal treatment of the Pt/CeO₂/Cu(111) sample are shown in Figure 1. A typical image representing the clean CeO₂(111)/Cu(111) film is displayed in Figure 1a. An average CeO₂(111) film thickness of 1.5 nm was estimated from the XPS data based on the attenuation of the Cu 2p substrate signals. In spite of a sharp (1.5×1.5) low-energy electron diffraction (LEED) pattern, STM reveals prominent irregularities in its topography. In particular, the sample shows small flat areas (Figure 1a, white arrows) and extended rough areas covered with

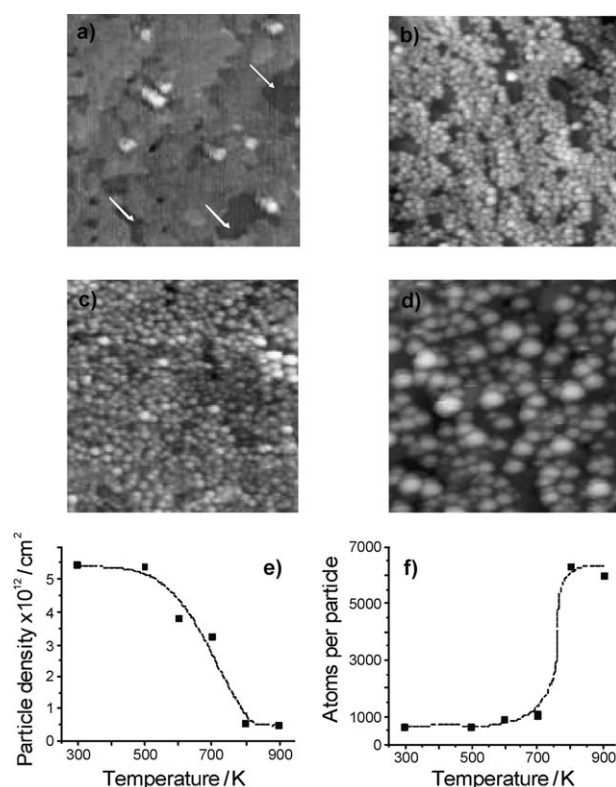


Figure 1. STM images observed on a) 1.5-nm-thick CeO₂(111)/Cu(111); b) Pt/CeO₂(111)/Cu(111) obtained by deposition of 0.5 nm Pt onto CeO₂(111)/Cu(111) at 300 K and subsequent annealing to 500 K; c) Pt/CeO₂(111)/Cu(111) annealed to 700 K; and d) Pt/CeO₂(111)/Cu(111) annealed to 900 K. The size of the STM images (a–d) is 150 × 150 nm². The tunneling parameters are: a) $U = 3.35$ V, $I = 0.3$ nA; b) $U = 3.35$ V, $I = 0.3$ nA; c) $U = 1.86$ V, $I = 0.63$ nA; d) $U = 2.91$ V, $I = 0.24$ nA. e) Evolution of Pt particle density and f) average number of Pt atoms per particle for Pt/CeO₂(111)/Cu(111) as a function of the annealing temperature.

small aggregates. Typical step heights are in good agreement with the expected heights of 3.1 and 6.3 Å for one monolayer (corresponding to an O–Ce–O trilayer) and double-layer steps (corresponding to two O–Ce–O trilayers) for CeO₂(111). The preparation is discussed in more detail elsewhere.^[33] It is important to mention, however, that there were no steps with heights lower than those of a O–Ce–O trilayer. Thinner patches may suggest missing layers of oxygen as reported previously^[34] and, therefore, may point to partially reduced cerium oxide.

In the next step, the oxidation state of cerium is analyzed by XPS. Figure 2 (top trace) shows a typical spectrum of the Ce 3d region for CeO₂/Cu(111) (estimated film thickness 1.5 nm). The spectrum is rather complex due to the occurrence of final-state effects (see, e.g., refs. [13,35]). For Ce⁴⁺, three spin–orbit split final states are populated, which according to standard nomenclature are denoted as ν – u , ν'' – u'' , and ν''' – u''' .^[13] These states correspond to different degrees of charge transfer between the Ce 4f levels and the O 2p bands, with the corresponding configurations $4f_2L^{n-2}$, $4f_1L^{n-1}$, and $4f_0L^n$ (here, L^{n-2} , L^{n-1} , and L^n designate the occupancy of the oxygen valence band, with L^n indicating full occupation).

Upon reduction, for example by release of lattice oxygen, part of the Ce⁴⁺ changes its oxidation state to Ce³⁺. For stoi-

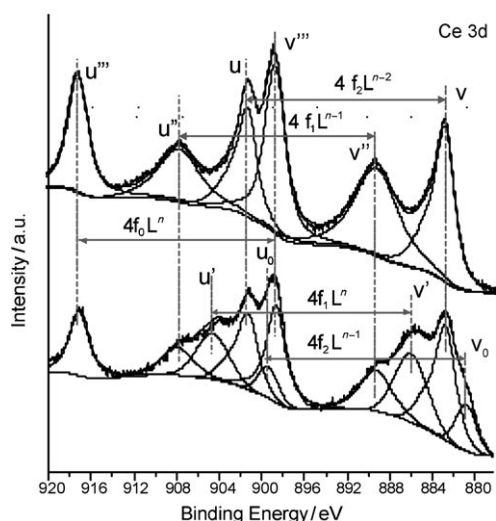


Figure 2. XP spectra of Ce 3d observed on stoichiometric (upper trace) and partially reduced cerium oxide films (bottom trace) on Cu(111). The spectrum of the stoichiometric cerium oxide comprises three doublets denoted as $v-u$, $v''-u''$, and $v'''-u'''$. They correspond to the $4f_2L^{n-2}$, $4f_1L^{n-1}$, and $4f_0L^n$ final states of the Ce^{4+} ion, respectively (see text for details). The spectrum of partially reduced cerium oxide (with about 30% Ce^{3+}) contains two additional doublets denoted as v_0-u_0 and $v'-u'$. They correspond to the $4f_2L^{n-1}$ and $4f_1L^n$ final states of the Ce^{3+} ion, respectively.

chiometric films, thermally activated reduction requires treatment at temperatures above 1000 K.^[31] The presence of Ce^{3+} gives rise to additional components in the X-ray photoelectron (XP) spectrum. A typical spectrum of partially reduced cerium oxide containing about 30% of Ce^{3+} is displayed in Figure 2 (bottom trace). Two additional doublets designated as v_0-u_0 and $v'-u'$ appear, which are associated with the final states $4f_2L^{n-1}$ and $4f_1L^n$, respectively.^[13,35] The cerium oxidation state is extracted from a numerical fit of the Ce 3d region, by taking into account the contributions from Ce^{3+} and Ce^{4+} . It should be pointed out that, immediately after preparation, the CeO_2 film on Cu(111) reveals Ce^{3+} concentrations which are below the detection limit of conventional XPS (around 2% Ce^{3+}). This finding is in good agreement with recent work by Matolin and co-workers, who showed that only traces of Ce^{3+} defects remain, which require more sensitive methods to be detected, such as RPES.^[30]

Next, we investigate the growth of Pt particles on the $CeO_2/Cu(111)$ model support. It turns out that the defect density of the cerium oxide surface greatly influences the nucleation of the deposited Pt layer. Figure 1b shows an STM image after deposition of Pt (nominal thickness 0.5 nm, 0.1 nm Pt corresponds to 6.8×10^{14} Pt atoms cm^{-2}). It is observed that nucleation with a high particle density occurs on the rough CeO_2 areas, whereas the nucleation density on the flat regions is substantially lower. Similar effects were previously observed for other metal/oxide systems (see, e.g., refs. [36–38]). A rough estimate of the particle size may be extracted from the STM images: an approximate Pt particle density of around $(5.4 \pm 1.0) \times 10^{12} cm^{-2}$ was obtained. Assuming near-unity sticking coefficients during Pt deposition on CeO_2 , this corresponds to particles containing on average 630 ± 100 Pt atoms per particle

or, assuming a half-spherical shape, to an average particle size of (3.3 ± 0.3) nm.

With respect to the present experiments, the thermal stability of the Pt/ $CeO_2/Cu(111)$ model catalyst is of utmost importance. Therefore, we tested the thermal stability by STM. Selected STM images after annealing are displayed in Figure 1c and d. The corresponding particle densities and sizes as a function of annealing temperature are shown in Figure 1e and f. It is observed that nearly no detectable changes occur up to 500 K. At temperatures up to 700 K, moderate morphological changes are observed. In particular, we detect some decrease in particle density, which is attributed to particle coalescence and Ostwald ripening. This observation is in good agreement with studies on the thermal stability of Pt particles on amorphous CeO_2 , also showing good stability up to around 700 K.^[39] At temperatures of 800 K and above, the system becomes unstable as indicated by the rapid decrease in particle density and increase in particle size (see Figures 1e,f).

In the next step we investigate the Pt–ceria interaction by XPS. The evolution of the Ce 3d and Pt 4f core-level spectra as a function of temperature is shown in Figure 3a and b. The top spectra in the Ce 3d and Pt 4f regions correspond to the situation immediately after Pt deposition at 300 K. In the Pt 4f region, a doublet develops at binding energies (BEs) of 71.3 and 74.5 eV (Figure 3b, ----) with a characteristic spin–orbit splitting of 3.2 eV. The Pt signals develop on the background of the Cu 2p doublet (Figure 3b, arrow), which contributes mainly to the high-energy side of the Pt 4f region. To disentangle the contributions from Cu and Pt, the spectra were fitted with a fixed Cu 2p peak shape, determined from the situation prior to Pt deposition. The Ce 3d spectrum in Figure 3a exhibits the characteristic components of Ce^{4+} (three doublets, see discussion above) arising from stoichiometric CeO_2 . The posi-

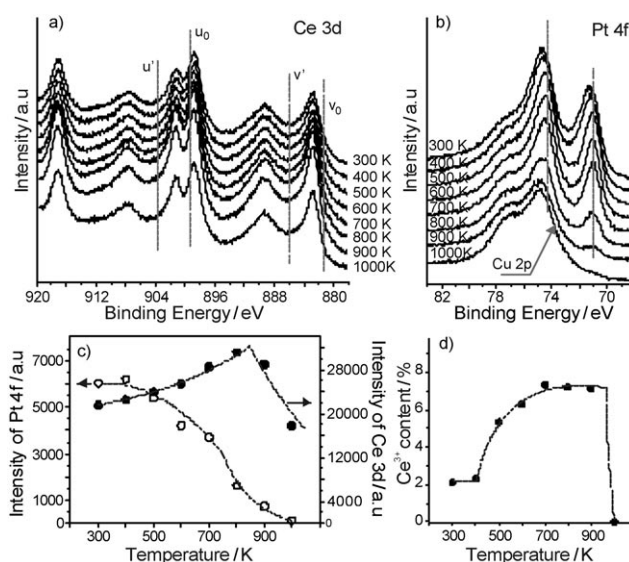


Figure 3. XP spectra of the a) Ce 3d and b) Pt 4f regions observed upon thermal treatment of the Pt/ $CeO_2/Cu(111)$ system. The system was obtained by deposition of Pt at 300 K. c) Development of the intensity in the Pt 4f and Ce 3d regions. d) Ce^{3+} content as derived from the intensity of the v_0-u_0 and $v'-u'$ doublets.

tions of potential contributions due to Ce^{3+} (v_0-u_0 and $v'-u'$ doublets) are indicated by dotted lines.

The Ce^{3+} contribution is too small to be noticed by eye and quantification requires numerical fitting to the complete Ce 3d region. The quantity of Ce^{3+} was, therefore, estimated by following a fitting procedure similar to that applied by Skála et al.^[23] The fraction of Ce^{3+} was then estimated from the ratio of the summed v_0-u_0 and $v'-u'$ doublet areas and the total area of the Ce 3d region.

It is observed that immediately after Pt deposition, some Ce^{3+} (approximately 2%) appears in the spectrum. Upon annealing, the intensity of the Pt 4f region decreases first slowly, then more rapidly at temperatures exceeding 700 K. Simultaneously, the Ce 3d intensity increases, before its breakdown at temperatures of 900 K and above (see Figure 3 c). On the basis of the STM observations (see above), we assign the initial increase/decrease in the Ce 3d/Pt 4f regions to thermally induced particle sintering, due to Ostwald ripening and coalescence. Thus, the intensities mainly follow the exposed fractions of Pt and Ce as a function of temperature. The change in intensity is accompanied by a BE shift of -0.2 eV and a narrowing of the Pt 4f peaks, which is in accordance with the typical size-dependent behavior of oxide-supported metal nanoparticles (for a detailed discussion see, e.g., refs. [40,41]). The more dramatic drop of the Pt 4f intensity around 800 K is associated with the structural instability of the Pt particles at these temperatures (see discussion above and Figure 1). Finally, the CeO_2 film itself becomes unstable at temperatures exceeding 900 K, which results in an instant drop of Ce 3d intensity.

The most interesting effect is related to the temperature dependence of the Ce^{3+} concentration (see Figure 3 d). As mentioned above, a small fraction of Ce^{3+} ions (2%) is detected immediately after deposition at 300 K. In a temperature region between 400 and 700 K, the Ce^{3+} fraction then progressively increases to a value of about 7%. At higher temperature, this value remains stable until the structural integrity of the CeO_2 film is lost (> 900 K).

Reduction of CeO_2 upon metal deposition was observed previously in several studies, for example, for $\text{Au/CeO}_2/\text{Cu}(111)$,^[24] $\text{Pd/CeO}_2/\text{Cu}(111)$,^[23] and $\text{Pt/CeO}_2/\text{Ru}(0001)$.^[42] As a potential origin of the effect we may invoke the activation of lattice oxygen by metal deposition, followed by reverse spillover of oxygen onto the Pt particles. Evidence for this effect was earlier reported for Rh/CeO_2 ^[28] and Pd/ceria-zirconia .^[29] Recently, a reverse spillover of lattice oxygen onto supported Pt particles was found, for example, for Pt/CeO_2 powder catalysts, based on isotopic exchange experiments.^[43] It should be pointed out, however, that Ce^{3+} formation may not necessarily involve oxygen mobility. Density functional theory (DFT) studies on the adsorption of Pt atoms on CeO_2 , for example, suggest that charge redistribution from Pt to neighboring Ce^{4+} centers may occur, thus reducing the oxidation state of the cation.^[44] In view of these considerations, we may tentatively suggest that the slight initial reduction observed upon Pt deposition at 300 K may be due to such a charge-transfer effect at the Pt/ CeO_2 interface, whereas the more pronounced reduction after annealing to 500 K may be due to oxygen reverse spillover

from CeO_2 to the Pt nanoparticles. This suggestion would be in accord within the temperature range previously reported for oxygen activation and reverse spillover on Rh/CeO_2 ^[28] or Pd/ceria-zirconia .^[29] In contrast to these systems, however, we do not observe any indication of oxidation of the Pt nanoparticles in the case of our model system. It should be pointed out that a different thermal behavior was observed for $\text{Au/CeO}_2/\text{Cu}(111)$,^[24] that is, a decrease of the Ce^{3+} concentration upon annealing. This would imply that on Au/CeO_2 , in contrast to Pt/CeO_2 , no reverse spillover occurs and that Ce^{4+} reduction on this system is purely due to an electronic interaction.

2.2. Adsorption of CH_4 on $\text{Pt/CeO}_2/\text{Cu}(111)$

In the next step we investigate the activation of methane on $\text{Pt/CeO}_2/\text{Cu}(111)$. Due to the low sticking coefficient of methane on Pt surfaces, we use a seeded supersonic beam to accelerate CH_4 in a mixture with He to a kinetic energy (KE) of 0.83 eV. For more details on the experimental setup and procedure, we refer to the previous work by Steinrück and co-workers, who used the same experimental setup to perform measurements on close-packed and stepped Pt single-crystal surfaces.^[8,9] The evolution of the Pt 4f and C 1s spectra from the $\text{Pt/CeO}_2/\text{Cu}(111)$ samples exposed to increasing doses of CH_4 is displayed in Figure 4 for two different sample temperatures, 300 (Figure 4 a,b) and 130 K (Figure 4 c,d). Immediately after sample preparation, three signals can be identified in the C 1s region, two sharp peaks at 284.4 and 286.7 eV and a broad feature at 289.1 eV. The latter is assigned to the Ce 4s signal which coincides with the C 1s region. The peaks at 284.4 and

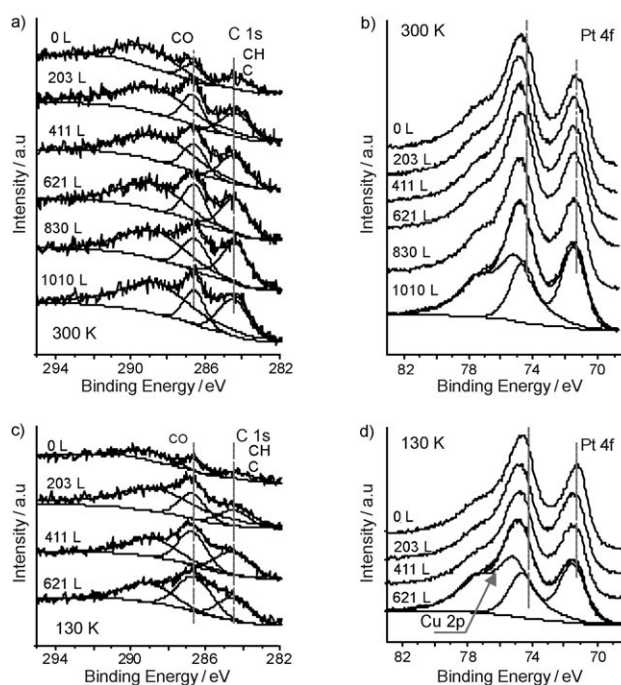


Figure 4. XPS spectra of the C 1s and Pt 4f regions, observed after the exposure of $\text{Pt/CeO}_2(111)/\text{Cu}(111)$ to increasing doses of CH_4 (MB, KE 0.83 eV) at sample temperatures of 300 (a,b) and 130 K (c,d). The positions of the C 1s signals of CO, CH, and C and the Pt 4f doublet are marked by dashed lines.

286.7 eV are assigned to C and CO contamination, respectively. The CO contamination grows during the exposure, and could not be avoided during the molecular beam (MB) experiment. The reason is that the experiment involves exposures to large total gas doses of around 10000 L from a high-temperature nozzle, always generating traces of CO.

During methane exposure, the most prominent change is observed for the feature at 284.4 eV, which continuously grows in intensity. It should be pointed out that no shoulder or component at lower BE is observed. The changes in the Pt 4f region are more subtle. Here, we observe a spin-orbit split doublet at 71.3 and 74.4 eV (Figure 4b,d). It overlaps with the Cu 2p signal, which was subtracted for fitting. Upon CH₄ exposure we identify a small shift of 0.10 and 0.15 eV to higher BE at 300 and 130 K, respectively.

The activated adsorption of methane was previously investigated by Steinrück and co-workers, both on Pt(111)^[8] and on stepped Pt surfaces, namely Pt(355) and Pt(322).^[9] Briefly, it was found that for methane adsorption on Pt(111) at KEs up to 0.83 eV, adsorption occurs via abstraction of a single hydrogen atom and formation of a stable methyl species (CH₃). The CH₃ species, which gives rise to a C 1s signal at 282.5 eV, decomposes at 260 K under further dehydrogenation and formation of CH (BE 283.6 eV). Simultaneously, partial recombination and evolution of CH₄ occurs. CH on Pt(111) was found to be stable up to 500 K, before total dehydrogenation to atomic carbon occurs (BE 284.0 eV). In addition, CH is the common product of methyl decomposition induced by X-ray irradiation even at low temperatures.^[8] CH₂, on the other hand, was never observed as a stable intermediate. On stepped Pt surfaces, dehydrogenation of both CH₃ and CH occurs at substantially lower temperatures (160 to 220 K for CH₃ dehydrogenation and 420 to 450 K for CH dehydrogenation^[8,9]), which suggests that the corresponding activation barriers are considerably reduced. To the best of our knowledge, no MB studies on methane activation on supported Pt nanoparticles have yet been performed. However, Tait et al. have investigated activated CH₄ adsorption on Pd nanoparticles supported on MgO(100).^[32] In this work, an enhanced sticking coefficient for CH₄ on Pd nanoparticles was found, which suggested that the initial activation barrier for abstraction of the first H atom may also be reduced.

On the basis of the single-crystal data, the C 1s signal at 284.4 eV for the present Pt/CeO₂/Cu(111) samples can be assigned to either atomic carbon or CH. DFT calculations, which are currently being performed, suggest a strongly reduced activation barrier for CH₃ dehydrogenation, but rather an enhanced barrier for CH dehydrogenation on Pt nanoparticles. These results will be discussed in detail in a forthcoming publication.^[45] Based on these results we tentatively assign the feature at 284.4 eV to CH on Pt nanoparticles. The slight shift to a higher BE in comparison to the single-crystal data is typical for oxide-supported metal particles and may be primarily attributed to the final-state coulomb charge (see, e.g., refs. [38,40,41]). The most surprising observation is, however, that for the Pt/CeO₂/Cu(111) samples no indication of the presence of stable CH₃ species is found, neither at 300 nor at 130 K. This suggests that on the Pt nanoparticles the activation

barrier for CH₃ dehydrogenation is drastically reduced. This conclusion appears not improbable considering an enhanced reactivity of the stepped Pt single-crystal surfaces, as discussed above.^[8,9] Both adsorption of CH species and the increasing coverage by CO as a contaminant give rise to a small shift of the Pt 4f surface core levels of 0.10 and 0.15 eV for exposure at 300 and 130 K, respectively. Again, we refer to a forthcoming publication for a detailed discussion of the energetics and kinetics of CH₄ activation on Pt nanoparticles.^[45]

Herein, the focus is on the role of the ceria support. Towards this aim, the corresponding Ce 3d and O 1s spectra have been analyzed in detail. Figure 5 summarizes the corresponding results for exposure to CH₄ at sample temperatures of 300 (Figure 5a,b) and 130 K (Figure 5c,d). Focusing on the Ce 3d spectra first, prominent changes involving the contributions of the v₀-u₀ and v'-u' doublets are apparent. The corresponding Ce³⁺ content as derived from a fitting procedure is displayed in Figure 5e. It is found that the Ce³⁺ fraction increases with increasing CH₄ dose. The effect is more pronounced, however, for adsorption at 300 K. In parallel with the Ce 3d levels, characteristic changes in the O 1s spectra are observed. Besides the main

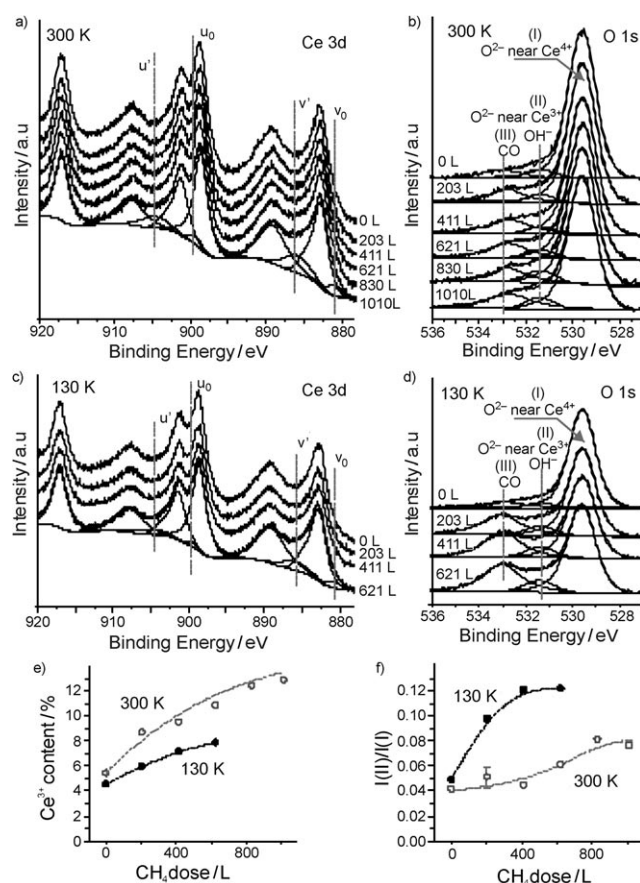


Figure 5. a–d) XP spectra of the Ce 3d and O 1s regions observed after the exposure of Pt/CeO₂(111)/Cu(111) to increasing doses of CH₄ (MB, KE 0.83 eV) at 300 K (a,b) and 130 K (c,d). The locations of the v₀-u₀ and v'-u' doublets (Ce³⁺) are labeled by dashed lines. For an assignment of the three components in the O 1s spectra, see the discussion in the text. e) Development of the Ce³⁺ content and f) the intensity ratio of O 1s component II with respect to component I as a function of exposure.

peak (Figure 5 b,d, peak I) due to O^{2-} near Ce^{4+} (BE 529.6 eV), two new features are observed at BEs of 531.4 (peak II) and 532.7 eV (peak III).

The latter feature (Figure 5 b,d, peak III) can be attributed to a contribution from CO contamination (see above). The BE is consistent with that reported for CO adsorption studies on Pt surfaces.^[46] The second peak at 531.4 eV (peak II) may contain several contributions. First, the peak will be partly due to oxygen located near Ce^{3+} centers. This feature is typical for partially reduced cerium oxide.^[47] An additional contribution may originate from the presence of OH groups on cerium oxide.^[48] A plot of the intensity ratio of peak II relative to the intensity of the main component (peak I) is displayed in Figure 5 f. Similarly to the Ce^{3+} signal, the feature increases in intensity with increasing methane exposure. However, an opposite trend is visible with respect to the dependence on the adsorption temperature. With increasing sample temperature, the intensity of the O 1s component II decreases, whereas the Ce^{3+} signal increases when rising from 130 to 300 K.

Based on the above assignment we suggest the following interpretation for these observations. From the C 1s spectra it was concluded that dehydrogenation to CH occurs upon methane activation. Reduction of Ce^{4+} may now occur as a result of hydrogen spillover from the Pt nanoparticles to the CeO_2 support. This process will lead to both the formation of OH groups and the reduction of Ce^{4+} to Ce^{3+} . The formation of the reductive O–H bonds on the surface of CeO_2 upon adsorption of hydrogen has been previously observed on similar systems such as Rh/ CeO_2 (see, e.g., refs. [13,49]). The fact that ceria reduction is observed at 130 K shows that hydrogen spillover has a low activation barrier and may, at least partially, occur even at low temperatures. This is in contrast to oxygen reverse spillover, which is only activated at elevated temperatures around 400 to 500 K (see Sect. 2.1). The stronger reduction at 300 K is attributed to a completion of hydrogen spillover, which requires slightly higher temperatures (as will be discussed below). With increasing temperature OH groups may be removed by water formation and desorption. Therefore, we attribute the decreasing shoulder (peak II) in the O 1s spectrum to water desorption starting at temperatures around 200 to 300 K (see discussion below). Note that this process leaves behind oxygen vacancies in the surface layer and Ce^{3+} ions, which remain visible in the Ce 3d spectrum.

2.3. Thermal Behavior, Hydrogen and Oxygen Spillover, and Carbon Removal

Finally, we investigate the thermal behavior of the Pt/ CeO_2 /Cu(111) model catalyst after methane activation. The evolution of the C 1s and Pt 4f spectra upon stepwise annealing after methane exposure at 300 and 130 K (from the MB, 0.83 eV KE) is shown in Figure 6. The corresponding Ce 3d and O 1s spectra are displayed in Figure 7.

We start by considering the C 1s spectra (Figure 6 a,c). The upper spectrum in both C 1s traces shows the initial state of the sample after exposure. Components at 284.4, 286.7, and a broad feature at 289.1 eV are observed, which are attributed to

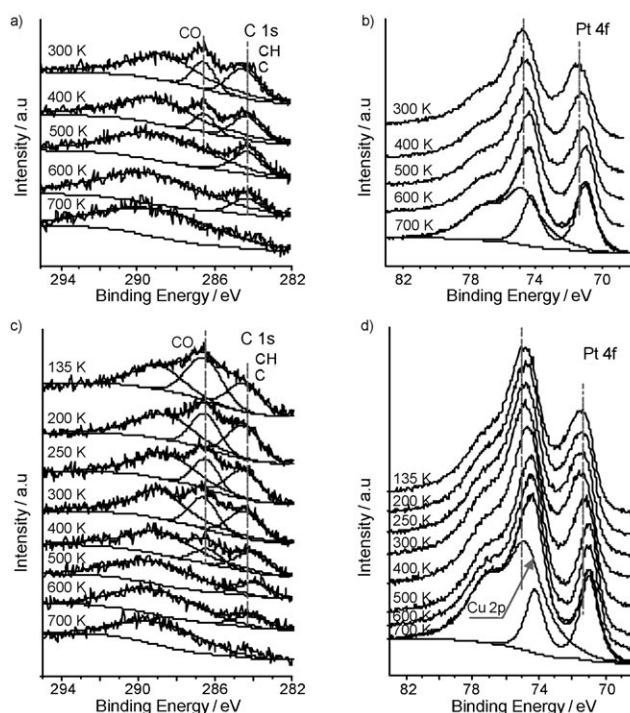


Figure 6. XP spectra of the a,c) C 1s and b,d) Pt 4f regions observed upon stepwise annealing of Pt/ CeO_2 (111)/Cu(111), subsequent to exposure to CH_4 at 300 (a,c) and 130 K (b,d). The positions of the C 1s signals of CO, CH, and C and the Pt 4f doublet are marked by dashed lines.

the C 1s signals of CH and CO as well as the Ce 4s background signal, respectively (see Sect. 2.2 for details). We observe that the CO feature decreases in intensity at 400 K and completely vanishes at 500 K. This effect is attributed to the oxidation of CO, possibly accompanied by CO desorption (see, e.g., refs. [50,51]). As will be shown below, the oxygen is supplied through reverse spillover by the ceria support. As pointed out before, we cannot differentiate between CH and atomic carbon in the present study due to the BE differences being too small. Based on single-crystal data (see discussion in Sect. 2.2) we may assume, however, that dehydrogenation of CH occurs in the temperature window between 400 and 500 K.^[8,9] This would imply that at 500 K and above, atomic C is the only species left on the Pt particles. At these temperatures, we notice a BE shift of around -0.3 eV, both in the C 1s and the Pt 4f levels (see Figure 6). Several effects may contribute to this shift, including the loss of co-adsorbed CO, a partial loss of CH, and a slight sintering of the Pt particles. The most interesting observation, however, is related to the behavior at even higher temperatures. We find that in the temperature region between 500 and 700 K, the remaining C 1s signal disappears completely. It should be pointed out that the model system preserves its structural integrity in this temperature region (see Sect. 2.1.) We may, therefore, conclude that the carbon is removed oxidatively via reaction with atomic oxygen, formation of CO/CO_2 , and desorption. The only source of available atomic oxygen is the ceria support, which supplies oxygen through reverse spillover.

To monitor the reduction and spillover processes involving the ceria support, we analyzed the Ce 3d and O 1s spectra (Figure 7). As described above, the oxidation state of the ceria support is extracted from the intensity of the v_0 – u_0 and v' – u' components in the Ce 3d region (Figure 7a,c). Additional information on the presence of both OH and Ce^{3+} can be derived from the corresponding shoulder (component II, 531.4 eV) in the O 1s signal (Figure 7b,d). (Note that components I and III in the O 1s region are again due to O^{2-} near Ce^{4+} and CO, respectively, and will not be discussed further; see Sect. 2.2 for details.) The result of fits of the corresponding regions are displayed in Figure 7e,f for samples prepared at both 130 and 300 K. We observe that the Ce^{3+} ion fraction increases upon annealing in two steps, one below 200 K and one in between 400 and 700 K (Figure 7e). After the complete removal of the carbon at 700 K, the Ce^{3+} fraction increases to values of 30%. Thus, the Ce^{3+} fraction is considerably higher than the maximum Ce^{3+} content observed after annealing of the adsorbate-free Pt/CeO₂/Cu(111) sample (7%, see discussion in Sect. 2.1). Note that the samples prepared by methane activation at 300 and 130 K exhibit a very similar behavior at temperatures of 300 K and above.

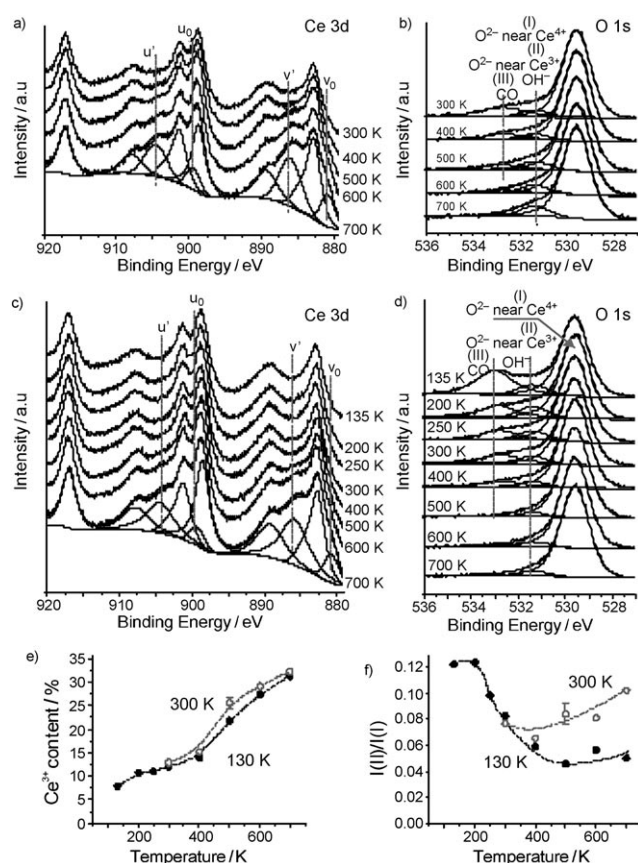


Figure 7. a–d) XPS spectra of the Ce 3d and O 1s regions observed upon stepwise annealing of Pt/CeO₂(111)/Cu(111) subsequent to exposure to CH₄ at 300 K (a,b) and at 130 K (c,d). The locations of the v_0 – u_0 and v' – u' doublets (Ce^{3+}) are labeled by dashed lines. For an assignment of the three components in the O 1s spectra, see the discussion in the text. e) Development of the Ce^{3+} content and f) the intensity ratio of O 1s component II with respect to component I as a function of annealing temperature.

The evolution of component II in the O 1s spectra again shows a behavior which is very different from that of the Ce^{3+} components (Figure 7f). We observe a slight increase in intensity from 130 to 200 K, before the intensity of the component sharply decreases up to temperatures of 400 K. At higher temperature (400 to 700 K), the intensity of the O 1s component II finally increases again.

Based on the previous discussion we assign the initial increase to the completion of hydrogen spillover from the Pt particles to the ceria support, which leads to the formation of OH groups and simultaneous reduction of the CeO₂ film. This observation shows that hydrogen spillover is highly facile and occurs even at low temperatures.^[52] The decrease in the intensity of O 1s component II in the temperature window between 200 and 400 K is then attributed to the decomposition of hydroxyl groups and the desorption of water (see Sect. 2.2 and cf. ref. [53]). In Sect. 2.1 we have shown that at temperatures between 400 and 500 K oxygen from the ceria support becomes mobile and may migrate to the Pt particles. As long as the Pt particles are free of adsorbates, this reverse-spillover process stops after mild reduction of the ceria. However, in the presence of reducing agents such as adsorbed CO or C, spillover oxygen will be continuously consumed. For Pt(111), the onset of CO oxidation is expected to appear around 400 K,^[50] whereas the onset for recombination of atomic carbon and oxygen is observed around 550 K.^[54] Both processes are facile and lead to consumption of oxygen on the Pt particles by CO₂ and/or CO production. Continuous supply of oxygen from the support via reverse spillover then finally leads to a complete removal of the carbonaceous species and to a drastic reduction of the ceria support.

3. Conclusions

We have performed a comprehensive study on the activation and dehydrogenation of methane on a Pt/CeO₂/Cu(111) model catalyst, mainly focusing on the role of the support with respect to hydrogen and oxygen spillover processes and self-cleaning from carbonaceous species.

- 1) Structure and growth of the Pt/CeO₂/Cu(111) model catalyst: The structure of the CeO₂/Cu(111) model support and the growth of Pt on CeO₂/Cu(111) was characterized by STM. It is shown that nucleation of Pt strongly depends on the defect density of the ceria film. The typical particle density was determined as $(5.4 \pm 1.0) \times 10^{12} \text{ cm}^{-2}$, which leads to average particle sizes around $(3.3 \pm 0.3) \text{ nm}$ (or 630 ± 100 Pt atoms per particle) at the nominal Pt coverages used in this study (0.5 nm).
- 2) Thermal stability of the Pt/CeO₂/Cu(111) model catalyst: The thermal behavior was investigated by STM and XPS. It is shown that the system maintains its structural integrity up to temperatures around 700 K with minor sintering of the Pt nanoparticles. At 800 to 900 K, diffusion of the Pt particles into the support occurs, followed by disintegration of the ceria thin film around 900 to 1000 K.

- 3) Metal-oxide interaction and oxygen reverse spillover on Pt/CeO₂/Cu(111): Immediately after deposition of Pt at 300 K, a slight reduction of the initially stoichiometric CeO₂ thin film is observed. We assign this effect to the metal-oxide interaction at the nanoparticle/support interface. At temperatures between 400 and 500 K, oxygen reverse spillover from the ceria support to the Pt particles is activated. This process gives rise to a more pronounced reduction of the CeO₂ thin film.
- 4) Methane activation on Pt/CeO₂/Cu(111): Methane activation was probed by means of MB experiments using high-KE CH₄ (0.83 eV). In contrast to the behavior on Pt single crystals, methane dehydrogenation immediately proceeds to CH, without detectable amounts of CH₃, even at sample temperatures of 130 K. This behavior indicates a strong modification of the activation barriers for the individual dehydrogenation steps on small particles.
- 5) Hydrogen spillover on Pt/CeO₂/Cu(111): Upon methane activation, spillover of hydrogen from the Pt particles to the CeO₂/Cu(111) support is observed, as indicated by the formation of hydroxyl groups on ceria. Hydrogen spillover is facile and occurs at 130 K, coming to completion at temperatures around 200 K. In the temperature region between 200 and 400 K, the hydrogen groups decompose leaving behind Ce³⁺ centers.
- 6) Formation and removal of carbonaceous species on Pt/CeO₂/Cu(111): Upon thermal treatment complete dehydrogenation of CH and formation of carbonaceous species occurs. These species react with oxygen supplied via reverse spillover from ceria in the temperature region between 500 and 700 K and desorb in the form of CO and/or CO₂. This self-cleaning process leaves behind a completely carbon-free surface and a strongly reduced ceria support containing up to 30% of Ce³⁺ ions.

Experimental Section

XPS studies were carried out in a UHV system designed for MB/XPS experiments at base pressures of around 1×10^{-10} mbar. The experimental setup consisted of an MB/XPS chamber and a separate preparation chamber. The chambers could be disconnected by a UHV valve and were both equipped with separate pumping lines and gas inlet systems. A motorized transfer rod facilitated fast axial movement of the sample between the chambers. The preparation chamber was equipped with two electron-beam evaporators (Focus EFM 3) for metal deposition, an ion gun, and a LEED optic. The analyzing chamber was equipped with a hemispherical electron-energy analyzer (Omicron EA 125 U7 HR) and a twin X-ray gun operating with Mg and Al anodes. Furthermore, a quadrupole mass spectrometer was available. A unique feature of the experimental setup was a supersonic MB subchamber, mounted at an angle of 45° with respect to the analyzer lens system. It allowed the generation of a collimated supersonic beam by expanding gases through a heatable 100-μm-diameter Mo nozzle. The beam was shaped by three successive differential pumping stages. The MB was passing the focal point of the analyzer, hence allowing for in situ XPS analysis during sample exposure. A beam flag mounted on a pneumatic feed-through in the second pumping stage al-

lowed for fast switching (<0.1 s) of the beam.^[55] In the current experiments, methane (99.995%, Linde) with a KE of 0.83 eV was used. The high-KE CH₄ was generated by expansion through a heated nozzle at 1273 K and seeding in He (99.9999%, Linde). In the current experiments a seeding ratio of 1:10 CH₄/He was used. For more details on the experimental procedure, refer to the literature.^[55] CH₄ and He gases were additionally cleaned by using cooling traps. Still, CO contamination generated in the nozzle could not be avoided due to the large gas exposure. Such contamination has already been observed in previous experiments using the same experimental setup.^[9]

The Pt/CeO₂/Cu(111) samples were prepared in several steps. First, the Cu(111) single crystal (Surface Preparation Laboratory) was cleaned by several cycles of Ar⁺ sputtering (at 300 K for 30 min, then at 873 K for 30 min) and annealing (723 K for 5 min) until no traces of carbon or any other contaminant was found in the XP spectra. Epitaxial layers of CeO₂ were grown on clean Cu(111) by PVD of Ce metal (Alfa Aesar, 99.9%) in an oxygen atmosphere ($p_{\text{O}_2} = 5 \times 10^{-7}$ mbar) at 523 K, followed by annealing of the films at 523 K in an oxygen atmosphere ($p_{\text{O}_2} = 5 \times 10^{-7}$ mbar) for 10 min. This preparation procedure followed the recipe previously described by Matolín et al.^[30,31] The method yielded a continuous CeO₂(111) film with a thickness of approximately 1.2 nm, as determined from the attenuation of the Cu 2p intensity. LEED observations on the prepared films confirmed epitaxial growth of CeO₂(111) with the characteristic (1.5×1.5) superstructure in relation to the Cu(111) substrate.

Pt was deposited onto the CeO₂/Cu(111) films by means of a commercial evaporator (Focus EFM 3) based on electron-beam heating of a Pt wire (Goodfellow, 99.99%). The sample was kept at 300 K during deposition. The nominal thickness of the deposited Pt layer was 0.5 nm, as determined by XPS.

The morphology of the CeO₂/Cu(111) and Pt/CeO₂/Cu(111) films were additionally characterized by STM, performed in a separate UHV chamber (base pressure below 1×10^{-10} mbar). The chamber was equipped with a commercial scanning tunneling microscope of beetle-type design (RHK Technology, Inc.), home-built LEED optics, standard facilities for surface cleaning, and two commercial electron-beam metal evaporators (Focus, EFM3). Electrochemically etched W tips were used for imaging the surfaces in constant-current mode at room temperature. Film thicknesses were calibrated by means of a quartz microbalance.

For the XPS experiments, Al_{Kα} radiation was applied to all the samples. The spectra were acquired at constant pass energy at an emission angle for the photoelectrons of 50° with respect to the sample normal. The spectra of Ce 3d, Pt 4f, C 1s, and O 1s were fitted with mixed Gaussian and Lorentzian line profiles (Voigt profile) after subtraction of a Shirley background, to account for the inelastic background. During the XPS experiments the sample temperature was controlled by a dc power supply passing a current through the sample. The actual temperature was measured by two K-type thermocouples connected at the edges of the sample. A stable temperature and fast cooling after the annealing steps were achieved by simultaneous resistive heating and cooling of the sample with a flow of liquid nitrogen.

Acknowledgements

The authors gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) within the ERACHEM

program ("NanoFunC" project) and additional support from the DFG within the Excellence Cluster "Engineering of Advanced Materials" in the framework of the excellence initiative. Furthermore, we acknowledge support by the Fonds der Chemischen Industrie, the DAAD (PPP, Acciones Integradas Hispano-Alemanas), and the European Union (COST D-41). We acknowledge the cooperation with the Lehrstuhl für Festkörperphysik at Friedrich-Alexander-Universität Erlangen-Nürnberg and the assistance of Dr. L. Hammer and Prof. Dr. M. A. Schneider in STM measurements. The authors are particularly thankful to Prof. Matolín (Charles University, Prague) for advising on the preparation of CeO₂ films on Cu(111).

Keywords: cerium oxide · heterogeneous catalysis · methane dehydrogenation · supported catalysts · platinum

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Received: August 25, 2009

Revised: October 16, 2010

Published online on January 27, 2010