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Article

Nanoscale architecture of ceria-based model catalysts: Pt–Co nanostructures on well-ordered CeO₂(111) thin films

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ABSTRACT

We have prepared and characterized atomically well-defined model systems for ceria-supported Pt–Co core-shell catalysts. Pt@Co and Co@Pt core-shell nanostructures were grown on well-ordered CeO₂(111) films on Cu(111) by physical vapour deposition of Pt and Co metals in ultrahigh vacuum and investigated by means of synchrotron radiation photoelectron spectroscopy and resonant photoemission spectroscopy. The deposition of Co onto CeO₂(111) yields Co–CeO₂(111) solid solution at low Co coverage (0.5 ML), followed by the growth of metallic Co nanoparticles at higher Co coverages. Both Pt@Co and Co@Pt model structures are stable against sintering in the temperature range between 300 and 500 K. After annealing at 500 K, the Pt@Co nanostructure contains nearly pure Co-shell while the Pt-shell in the Co@Pt is partially covered by metallic Co. Above 550 K, the re-ordering in the near surface regions yields a subsurface Pt–Co alloy and Pt-rich shells in both Pt@Co and Co@Pt nanostructures. In the case of Co@Pt nanoparticles, the chemical ordering in the near surface region depends on the initial thickness of the deposited Pt-shell. Annealing of the Co@Pt nanostructures in the presence of O₂ triggers the decomposition of Pt–Co alloy along with the oxidation of Co, regardless of the thickness of the initial Pt-shell. Progressive oxidation of Co coupled with adsorbate-induced Co segregation leads to the formation of thick CoO layers on the surfaces of the supported Co@Pt nanostructures. This process is accompanied by the disintegration of the CeO₂(111) film and encapsulation of oxidized Co@Pt nanostructures by CeO₂ upon annealing in O₂ above 550 K. Notably, during oxidation and reduction cycles with O₂ and H₂ at different temperatures, the changes in the structure and chemical composition of supported Co@Pt nanostructures were driven mainly by oxidation while reduction treatments had little effect regardless of the initial thickness of the Pt-shell.

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1. Introduction

The development of active and durable catalysts with

reduced Pt content is of paramount importance for commercialization of proton exchange membrane fuel cells (PEMFCs) [1–3]. Recently, significant progress was made by

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using atomically dispersed Pt as an anode catalyst for the direct hydrogen PEMFCs [4]. However, due to the slow kinetics of the oxygen reduction reaction (ORR) at the cathode, the cathode catalysts contain much higher quantities of Pt. Recent studies suggested that alloying Pt with a second, less expensive metal leads to synergetic improvements of the catalyst performance while significantly reducing the Pt loading [5–9]. The major effect is achieved by the formation of core–shell nanostructures, where Pt forms a thin shell over the core of an inexpensive metal [7,8]. Among the studied bimetallic catalysts, Pt–Co systems demonstrated the highest activity for ORR [5]. It was suggested that the improvements in ORR activity are associated with strain effects, i.e. the changes in Pt–Pt bond distances, and the electronic effects arising from bimetallic interactions between the Pt and the Co metals [9–14]. The corresponding effects have been investigated as a function of Pt–Co alloy stoichiometry, the structure, and the composition of core–shell nanostructures supported on carbon [15–19]. However, the analysis of the electrochemically treated Pt–Co systems revealed structural instabilities associated with Ostwald ripening, aggregation of supported nanostructures, and leaching of Co [6,7,17,20]. It was found that the most active and stable Pt–Co systems consisted of Pt₃Co@Pt or Co@Pt core–shell nanostructures with 2–3 atomic layers thick Pt-shell [5,6,21].

With regard to the agglomeration, several strategies were suggested including encapsulation of core–shell nanostructures by sandwich-like carbon sheets [22] and the anchoring of supported nanostructures on functional oxides [23,24]. In particular, the use of reducible oxides as supports, e.g. CeO₂, improves the stability of supported noble nanoparticles against sintering [25,26]. The intrinsic property of CeO₂-based materials is their oxygen storage capacity associated with the redox conversion between the oxidations state Ce⁴⁺ and Ce³⁺ during release and uptake of oxygen [27,28]. In the presence of supported noble metal nanoparticles, e.g. Pt, electronic metal–support interactions (EMSI) give rise to charge transfer between the supported nanoparticle and the support [29]. The magnitude of the charge transfer depends on the size of the supported nanoparticles and the stoichiometry of the support. Therefore, EMSI represents a tunable parameter controlling the oxidation state and, as a result, the reactivity of supported nanoparticles [29]. Additionally, the CeO₂-based materials participate in chemical reactions by providing active oxygen species to the surface of supported nanoparticles by means of reverse oxygen spillover [30].

In the present paper, we employ well-ordered CeO₂(111) films as a functional support for model Co@Pt and Pt@Co core–shell nanostructures. The thermal stability of supported nanostructures is discussed with respect to segregation phenomena and sintering of the nanoparticles under different experimental conditions. The work provides an insight into the thermodynamically driven restructuring phenomena in supported Pt–Co nanostructures.

2. Experimental

High-resolution synchrotron radiation photoelectron spectroscopy (SRPES) and resonant photoemission spectroscopy (RPES) experiments were performed at the Materials Science Beamline (MSB), Elettra synchrotron light facility in Trieste, Italy. The MSB, with a bending magnet source provided synchrotron light in the energy range of 21–1000 eV. The UHV end-station (base pressure 2×10^{-10} mbar) was equipped with a multichannel electron energy analyzer (Specs Phoibos 150), a rear view low energy electron diffraction (LEED) optics, a sputter gun (Ar), and a gas inlet system for O₂ and H₂. The basic setup of the chamber included a dual Mg/Al X-ray source. Additionally, three electron-beam evaporators for the deposition of Ce, Pt, and Co metals were installed.

Three types of model catalysts including supported Co nanoparticles, Pt@Co (Pt core, Co shell), and Co@Pt (Co core, Pt shell) nanostructures were prepared on well-ordered CeO₂(111) films grown on a Cu(111) substrate. First, Cu(111) (MaTecK GmbH, 99.999%) was cleaned by several cycles of Ar⁺ sputtering (300 K, 60 min) and annealing (723 K, 5 min) until no traces of carbon or any other contaminant were found in the photoelectron spectra. Then, an epitaxial CeO₂(111) layer was deposited onto the clean Cu(111) substrate by physical vapor deposition (PVD) of Ce metal (Goodfellow, 99.99%) in an oxygen atmosphere ($p_{O_2} = 5 \times 10^{-7}$ mbar, Linde, 99.999%) at 523 K. This preparation method [31] yielded a continuous [32], stoichiometric CeO₂(111) film with a thickness of 2.0 nm as determined from the attenuation of the Cu 2p_{3/2} intensity. Co nanoparticles were prepared by means of PVD of Co metal (Goodfellow, 99.99%) in UHV onto the CeO₂(111)/Cu(111) at 300 K. The supported Pt@Co and Co@Pt core–shell nanoparticles were prepared by PVD of Co metal onto Pt/CeO₂(111) and by PVD of Pt metal onto Co/CeO₂(111), respectively. The corresponding Pt/CeO₂(111) and Co/CeO₂(111) were prepared by PVD of Pt (nominal thickness 0.37 nm, 1.6 ML, where 1 ML = 0.2266 nm) and Co (nominal thickness 0.51 nm, 2.5 ML, where 1 ML = 0.2035 nm), respectively, onto CeO₂(111) films in UHV at 300 K. Here, 1 ML is defined as the interplanar distance between (111) crystal planes in Pt metal and (0001) crystal planes in Co metal. In the case of the Pt/CeO₂(111) system, the supported Pt particles were 3.0 nm in diameter [29]. Prior to the deposition of the Co-shell, the Pt/CeO₂(111) was briefly annealed to 500 K in order to remove CO contamination. The deposition rates of Co and Pt metals were 0.08 and 0.03 ML $\times$ min^{−1}, respectively.

The Co 2p, Pt 4f, C 1s, and O 1s spectra were acquired with photon energies of 930, 180, 410, and 650 eV, respectively. The binding energies in the spectra acquired with synchrotron radiation were calibrated with respect to the Fermi level. Additionally, Al K α radiation (1486.6 eV) was used to measure O 1s, Ce 3d, Co 2p, Pt 4f, and Cu 2p_{3/2} core levels. All spectra were acquired at constant pass energy and at an emission angle for the photoelectrons of 20°/60° and 0° with respect to the sample normal, while using the x-ray source and synchrotron radiation, respectively. The spectral components in Pt 4f spectra were fitted with an asymmetric Doniach–Šunjić function convoluted with a Gaussian profile. All components in the Pt 4f spectra were fitted by doublet peaks with a spin-orbit

splitting of 3.3 eV. Co 2*p* spectra were fitted with Voigt profiles. Co 2*p* spectra obtained at low Co coverages (0.12 nm, 0.6 ML) and after the annealing above 500 K were fitted after subtraction of a composite background. The composite background consisted of a baseline spectrum obtained prior to Co deposition and a Shirley background. The use of the composite background was necessary to compensate for the complex shape of the background in the Co 2*p* region.

Valence band spectra were acquired at three different photon energies, 121.4, 124.8, and 115.0 eV. Analysis of the spectra obtained with these photon energies forms the basis of RPES on ceria-based materials [29,33]. Briefly, RPES is based on measuring the valence band photoemission spectra at photon energies corresponding to the 4*d*→4*f* resonance either in the Ce³⁺ or the Ce⁴⁺ ions. The Ce³⁺ resonance at a photon energy of 121.4 eV is caused by a super Coster–Kronig decay involving electron emission from Ce 4*f* states located about 1.4 eV below the Fermi edge. The Ce⁴⁺ resonance at a photon energy of 124.8 eV involves emission of O 2*p* electrons (hybridized with Ce states) from the valence band around 4.0 eV. The valence band spectrum obtained with a photon energy of 115 eV corresponds to the ‘off-resonance’ condition. The resonant enhancements for Ce³⁺ and Ce⁴⁺ (denoted as D(Ce³⁺) and D(Ce⁴⁺), respectively) are quantified by calculating the intensity difference between the corresponding features on- and off-resonance. The ratio between the corresponding resonant intensities, D(Ce³⁺)/D(Ce⁴⁺), denoted as a resonant enhancement ratio (RER) is a direct measure of the degree of reduction of cerium oxide and can be used to quantify the concentration of Ce³⁺ ions in the films [29]. Earlier we determined that the RER scales with the Ce³⁺/Ce⁴⁺ concentration ratio, $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$, by a factor of 5.5 [29]. All SRPES data were processed using KolXPD fitting software [34]. The values of total spectral resolution were 1 eV (Al *K_α*, $h\nu = 930$ eV), 200 meV ($h\nu = 115\text{--}180$ eV), 400 meV ($h\nu = 410$ eV), 650 meV ($h\nu = 650$ eV). During the experiment, the sample temperature was controlled by a DC power supply passing a current through Ta wires holding the sample. Temperatures were monitored by a K-type thermocouple attached to the back of the sample. In the oxidation and reduction cycles, the Co@Pt core-shell nanostructures were consecutively exposed to 50 L of O₂ and 50 L of H₂ (1 Langmuir (L) = 1.33×10^{-6} mbar·s) at constant temperatures between 110 and 750 K. The partial pressure of O₂ and H₂ during the exposure cycles was 2.66×10^{-7} mbar.

3. Results and discussion

3.1. Co nanoparticles on CeO₂(111)

The evolution of the Co 2*p* spectra upon stepwise deposition of Co onto the well-ordered CeO₂(111)/Cu(111) film at 300 K in UHV is shown in Fig. 1a. At the limit of low Co coverage, three doublet peaks were resolved in the Co 2*p* spectra at 780.8 (Co 2*p*_{3/2}), 782.9 (Co 2*p*_{3/2}), and 787.0 eV (Co 2*p*_{3/2}). In line with the work of Biesinger et al. [35], we associate all three peaks with the formation of Co²⁺ ions. The complex structure of the Co 2*p*

spectra results from the multiplet splitting and shake-up satellites typical for the 3*d* transition metal atoms containing unpaired electrons [35]. Accordingly, two doublet peaks labeled as Co²⁺ (Fig. 1a) are associated with the emission from Co 2*p* core levels while the broad doublet peak labeled as sat(Co²⁺) (Fig. 1a) is a shake-up satellite. At higher Co coverage, these are accompanied by an additional doublet peak at 778.6 eV (Co 2*p*_{3/2}) and two small peaks at 781.5 (Co 2*p*_{3/2}) and 783.5 eV (Co 2*p*_{3/2}) associated with the growth of metallic Co nanoparticles. Here, the main peak labeled as Co⁰ (Fig. 1a) is associated with the emission from the Co 2*p* core level. Two minor peaks associated with the characteristic loss features were added to resemble the shape of the Co 2*p* spectrum of metallic Co in accordance with the fitting procedure recommended by Biesinger et al. [35]. The formation of Co²⁺ ions triggers a reduction of the CeO₂(111) film associated with a change of the oxidation state of Ce⁴⁺ cations to Ce³⁺. Specifically, the formation of one Co²⁺ ion leads to the reduction of two Ce⁴⁺ cations to Ce³⁺. The development of the Ce³⁺/Ce⁴⁺ concentration ratio as determined by means of RPES, $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$, is plotted in Fig. 1d as a function of the nominal Co thickness. We note that the $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ ratio increases up to 0.43 at a nominal Co thickness of 0.8 ML. This corresponds to the stoichiometry CeO_{1.85}. Depth profiling of the Ce³⁺ and Co²⁺ distributions suggests that these ions are mostly located at the surface of the CeO₂(111) film (data are not shown). The deposition of a higher amount of Co leads to a slight re-oxidation of cerium oxide yielding a final stoichiometry CeO_{1.86} at a nominal Co thickness of 2.9 ML. The interaction of cobalt with thin films of cerium oxide was investigated earlier [36,37]. In particular, the formation of Co²⁺ associated with the partial reduction of cerium oxide was reported at Co coverages below 0.7 ML. At Co coverages above 0.7 ML, the growth of metallic Co in the form of three-dimensional nanoparticles was observed [37]. In the present work, the onset of metallic Co formation at 0.6 ML is in a good agreement with these observations. We note that the formation of metallic Co begins once the formation of Co²⁺ stops and the degree of the reduction of cerium oxide reaches saturation. With respect to the nature of the Co²⁺ species, a two-dimensional growth of CoO clusters was suggested earlier despite the unfavorable thermodynamics [36]. The authors [36] argued that formation of CoO becomes feasible due to the nanostructured nature of thin CeO₂ films. Alternatively, the formation of Co²⁺ species is also consistent with the formation of solid Co–CeO₂ solution in a manner similar to the behavior observed for Sn-doped and Ga-doped CeO₂ [38–41]. In fact, stable solid solution phases with a uniform dispersion of Co in the CeO₂ lattice were observed in Co/CeO₂ catalysts prepared by means of the sol–gel synthesis [42]. We note that three-fold adsorption sites for Co²⁺ (tetrahedral coordination) are available at the CeO₂(111) surface. A likely scenario involves the growth of metallic Co nanoparticles supported on a one monolayer-thick Co–CeO₂ solid solution.

3.2. Pt@Co nanostructure on CeO₂(111)

Fig. 1. The evolution of Co 2p spectra (a–c) and concentration ratio $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ (d–f) upon stepwise deposition of Co onto (a, d) $\text{CeO}_2(111)$ and (b, e) Pt/ $\text{CeO}_2(111)$, and Pt deposition onto (c, f) Co/ $\text{CeO}_2(111)$ at 300 K in UHV. The ball models illustrate the morphology of the Co nanoparticles (a), Pt@Co (b), and Co@Pt (c) core-shell nanostructures supported on the $\text{CeO}_2(111)$ film. The blue, green, red, and ivory balls represent Pt, Co, O, and Ce atoms, respectively.

Pt@Co nanostructures were prepared by means of Co deposition onto Pt nanoparticles supported on a well-ordered $\text{CeO}_2(111)/\text{Cu}(111)$ film at 300 K in UHV. The nominal Pt thickness of 0.37 nm used in the experiments corresponds to the growth of metallic Pt nanoparticles of 3.0 nm diameter [29]. Note that the deposition of Pt nanoparticles leads to a moderate reduction of $\text{CeO}_2(111)$ film due to the EMSI [29]. This results in an increase of $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ to 0.05. The development of the Co 2p spectra is shown in Fig. 1b. The spectral contributions from Co^{2+} and metallic Co^0 emerge simultaneously in the Co 2p spectra and grow as a function of the nominal Co thickness. The increase of $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ (Fig. 1e) is associated with the partial reduction of $\text{CeO}_2(111)$ caused by the formation of Co^{2+} ions. Notably, the final stoichiometry of $\text{CeO}_{1.86}$ is similar to the one obtained after the deposition of Co nanoparticles onto $\text{CeO}_2(111)$ (see Section 3.1). The

corresponding Pt 4f spectra are shown in Fig. 2a. Prior to Co deposition, the spectrum is dominated by the peak at 70.9 eV (Pt 4f_{7/2}) consistent with the formation of metallic Pt nanoparticles. The Co deposition gives rise to a new component at 71.8 eV (Pt 4f_{7/2}) which shifts to 72.1 eV with increasing amount of deposited Co. This is accompanied by a strong attenuation and a shift of the metallic Pt⁰ contribution to 71.3 eV. We associate the new component with the formation of solid solution at the Pt–Co interface.

This assignment is in line with the development of the intensities of the corresponding Pt–Co interface and metallic Pt⁰ contributions (Fig. 2c). In particular, the intensity of the Pt–Co interface contribution increases with increasing amount of Co deposited until it saturates at 0.8 ML of Co and decreases thereafter at higher Co thickness. According to the degree of attenuation of the total Pt 4f signal, the thickness of the

Fig. 2. The evolution of the Pt 4f spectra (a, b) and the integrated intensities (c, d) of metallic Pt⁰ (red squares), Pt–Co interface (green circles), and the total Pt 4f signal (black triangles) upon stepwise deposition of Co onto (a, c) Pt/CeO₂(111) and Pt deposition onto (b, d) Co/CeO₂(111) at 300 K in UHV. The ball models demonstrate the morphology of Pt@Co (a) and Co@Pt (b) core–shell nanostructures supported on the CeO₂(111) film. The blue green, red, and ivory balls represent Pt, Co, O, and Ce atoms, respectively.

deposited Co-shell is 2.5 ML. Considering the total amount of Co deposited, we determine that 0.5 ML of Co is converted into Co²⁺ upon interaction with CeO₂(111) substrate.

The structure and chemical composition of Pt–Co interface was investigated by Saint-Lager et al. [43]. The authors reported that a thin Co film (3 ML) deposited on Pt(111) at room temperature forms a sharp interface without any detectable signs of Pt–Co alloying. Progressive alloying was observed by the authors [43] only upon annealing. Therefore, we may speculate that the origin of the Pt–Co interface contribution in supported Pt@Co nanostructure could be associated with the minor Pt–Co intermixing upon Co deposition. Based on the Pt–Co phase diagram [44], the formation of a solid solution is favorable during stepwise deposition of Co onto Pt nanoparticles but it is kinetically hindered at 300 K.

3.3. Co@Pt nanostructure on CeO₂(111)

Co@Pt nanostructures were prepared by means of Pt deposition onto Co nanoparticles (nominal Co thickness 0.51 nm, 2.5 ML) supported on a well-ordered CeO₂(111)/Cu(111)

film at 300 K in UHV. The development of the Co 2p spectra is plotted in Fig. 1c as a function of nominal Pt thickness. We note that the deposition of Co nanoparticles led to a partial reduction of the CeO₂(111) film due to the formation of Co²⁺ as discussed in Section 3.1. The corresponding $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ ratio (see Fig. 1f) was 0.45 yielding a stoichiometry CeO_{1.85}. Pt deposition led to a decrease of $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ ratio due to partial re-oxidation of cerium oxide. Following the deposition of 1.5 ML of Pt, the final stoichiometry of cerium oxide was CeO_{1.93}. We believe that the mechanism of Co²⁺ reduction is associated with the reactive metal–support interaction (RMSI) [45,46] between the Pt and the Co–CeO₂ solid solution coupled with the reduction of Co²⁺ to Co⁰ followed by its diffusion to Pt. The similar effect was also observed upon deposition of Pt onto Sn-doped CeO₂(111) film at 300 K in UHV [45]. The reactive interaction of Pt with Sn²⁺ led to the reduction of Sn²⁺ yielding supported Pt–Sn nanoalloys. This process was accompanied by re-oxidation of cerium oxide.

The evolution of the Pt 4f spectra is shown in Fig. 2b. Two doublet peaks emerge at 71.3 (Pt 4f_{7/2}) and 72.0 eV (Pt 4f_{5/2}) associated with metallic Pt⁰ and Pt–Co interface contributions, respectively. The assignment of the Pt 4f peaks is in line with

the evolution of their intensities shown in Fig. 2d. The intensities of both contributions increase with increasing amount of deposited Pt. However, the increase of Pt–Co interface contribution is much slower with respect to Pt⁰. Still, despite the significant attenuation, the Pt–Co interface signal shows a steady growth up to 1.5 ML of Pt.

Cabeza et al. [47] investigated the growth and the structure of thin platinum films deposited on Co(0001). The authors reported coherent epitaxial growth of Pt film without Pt–Co alloying. The stability of the Pt films with respect to the alloy formation was found to be a function of Pt film thickness. Hence, if the first Pt ML has a high resistance to alloy formation, a growth of a second ML destabilizes the Pt films and facilitates alloying. However, a limited Pt–Co intermixing in the first Pt ML was also reported [48,49]. In fact, based on the Pt–Co phase diagram [44], the formation of a solid solution is also favorable during stepwise deposition of Pt onto Co nanoparticles at 300 K. In general, the association of the Pt–Co interface contribution with a minor Pt–Co intermixing at 300 K appears reasonable for both Pt@Co and Co@Pt nanostructures.

3.4. Thermal stability of supported Co, Pt@Co, and Co@Pt nanostructures

The thermal stability of the Co, Pt@Co, and Co@Pt nanostructures supported on CeO₂(111) were investigated upon annealing in UHV. We first established the stability regions of Co-core and Pt-core nanoparticles supported on CeO₂(111) films. Earlier, we reported that the morphology of Pt nanoparticles supported on CeO₂(111) is stable upon annealing up to 500 K [50]. At temperatures up to 700 K, moderate morphological changes occur that are associated with particle coalescence and Ostwald ripening [50].

With respect to the stability of the supported Co nanoparticles, we analyzed the Co 2*p* spectra plotted in Fig. 3a along with the integrated intensity of the metallic Co⁰ contribution and the $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ ratio plotted in Figs. 3d and 3g, respectively. Annealing of Co nanoparticles supported on CeO₂(111) resulted in a decrease of the Co 2*p* intensity (Fig. 3a). According to the evolution of the metallic Co⁰ contribution, the Co nanoparticles are fairly stable up to 500 K. Above 500 K, the Co⁰ intensity rapidly decreases due to sintering of supported Co nanoparticles [36,37].

In the next step, we compared the evolution of metallic Co⁰ 2*p* and Pt 4*f* intensities on two core-shell nanostructures, Pt@Co and Co@Pt, within the stability regions of Pt/CeO₂(111) and Co/CeO₂(111) (300–500 K). The corresponding Co 2*p* spectra, along with the integrated intensities of the metallic Co⁰ contributions and $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ ratios, are plotted in Figs. 3b–3c, 3e–3f, and 3h–3i, respectively. The corresponding Pt 4*f* spectra, along with the evolution of integrated total Pt 4*f* intensities, are shown in Figs. 4a–4b and 4c–4d, respectively. Annealing of the supported Pt@Co nanostructure up to 500 K leads to a slight decrease of metallic Co⁰ signal (Fig. 3e) and a slight increase of total Pt 4*f* intensity (Fig. 4c). In contrast, upon annealing of the supported Co@Pt nanostructure, the intensity of the metallic Co⁰ signal increases considerably (Fig. 3f) while

the total Pt 4*f* intensity decreases (Fig. 4d). This behavior suggests that annealing leads to rearrangements in both Pt@Co and Co@Pt nanostructures. Remarkably, the Pt 4*f* component associated with the Pt–Co interface gradually decreases and practically vanishes at 500 K on both the Pt@Co and the Co@Pt nanostructures. This behavior suggests that the shells and cores consist of nearly pure metallic Co⁰ and Pt⁰ on Pt@Co and Co@Pt nanostructures, respectively. We assume that upon annealing to 500 K, the Pt (Co) atoms with a large number of Co (Pt) neighbors, i.e. these at the ‘solid-solution-like’ Pt–Co interface, will dissolve deeper into the core and will not be detected anymore at a surface sensitive photon energy of 180 eV.

In the case of the Pt@Co nanostructure, our observations correspond well with the behavior of thin Co film deposited on Pt(111) [43]. In fact, the decrease of the Pt–Co interface signal (Fig. 4a) suggests the formation of a sharp interface between Pt and Co layers with, virtually, no Pt–Co intermixing. The slight increase of Pt⁰ intensity along with a slight decrease of Co⁰ intensity can be related to the rearrangements in Co shell, e.g. smoothening, or minor segregation of Pt at the surface of the Pt@Co nanostructure.

In the case of Co@Pt nanostructure, the decrease of total Pt 4*f* intensity along with the increase of Co⁰ signal suggests a segregation of Co⁰ at the surface. At the same time, the decrease of the Pt–Co interface contribution (Fig. 4b) points to the formation of a sharp interface. The increase of the Co⁰ concentration upon annealing to 500 K cannot be explained by Co segregation from the Co-core. Note that strong mobility of Co atoms would lead to formation of Pt–Co alloy phases (which in fact only occurs above 500 K irrespective of the crystallographic orientation of the Co substrate [51]). Therefore, we may speculate, that the source of Co⁰ could be the Co–CeO₂ solid solution formed during the preparation of the model system (see Section 3.1).

In fact, a decrease of the $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ ratio upon annealing to 500 K suggests the reduction of Co²⁺ and the re-oxidation of cerium oxide in all three systems, Co, Pt@Co, and Co@Pt (see Figs. 3d–3f, respectively). In earlier study [37], the corresponding process was associated with the migration of Co²⁺ species into the bulk of the CeO₂(111) film followed by their dissolution in Cu(111) substrate. However, in the case of Co@Pt nanostructure, the situation is different. As discussed in Section 3.3, the RMSI triggers the conversion of Co²⁺ species to Co⁰ already at 300 K. The same process could be initiated by annealing leading to conversion of the remaining Co²⁺ species to Co⁰ followed by their diffusion onto the Co@Pt nanostructure. As a result, the Co@Pt nanostructure is most likely covered by metallic Co⁰ in the form of patches, adsorbed Co atoms, or Co inclusions into the Pt shell. In all cases, the spectral contribution from the Pt atoms with low number of Co neighbors will not be distinguishable from the main Pt⁰ signal. We believe that this process could be avoided by annealing of the Co/CeO₂(111) to 500 K prior to the deposition of the Pt-shell.

Above 500 K, the intensities of Co⁰ contributions from the supported Co, Pt@Co, and Co@Pt nanostructures rapidly

Fig. 3. The evolution of Co 2p spectra (a–c), the integrated intensity of metallic Co contribution in Co 2p spectra, $I(\text{Co}^0)$ (d–f), and the concentration ratio $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ (g–i) upon annealing of Co/CeO₂(111) (a, d, g), Pt@Co/CeO₂(111) (b, e, h), and Co@Pt/CeO₂(111) (c, f, i) in UHV. The ball models demonstrate the morphology of Co nanoparticles (a, g), Pt@Co (b, h) and Co@Pt (c, i) core–shell nanostructures supported on CeO₂(111) film before (a–c) and after annealing to 500 K (g–i). The blue, green, red, and ivory balls represent Pt, Co, O, and Ce atoms, respectively.

decrease due to sintering (see Figs. 3g–3i). Notably, the $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ ratios increase on both Pt@Co and Co@Pt nanostructures (Figs. 3h–3i) due to the onset of oxygen reverse spillover observed earlier in the Pt/CeO₂(111) system [30]. The corresponding phenomenon is associated with the release of lattice oxygen followed by its diffusion onto the Pt@Co and Co@Pt nanostructures. In contrast, the $n(\text{Ce}^{3+})/n(\text{Ce}^{4+})$ ratio remains practically unchanged upon annealing of Co/CeO₂(111) above 500 K (Fig. 3g). This behavior suggests that the oxygen reverse spillover does not occur in the Co/CeO₂(111) system.

In the case of the Pt@Co nanostructure, we observed a sharp increase of the total Pt 4f intensity up to 600 K followed by its decrease at higher temperature. On Co@Pt nanostructure, the total Pt intensity continues to decrease gradually. However, a similarity between the two supported Pt@Co and Co@Pt nanostructures is the emergence of a doublet at 71.5 eV (Pt 4f_{7/2}) upon annealing above 550 K. We assign the corresponding doublet to the formation of Pt–Co alloy.

In the case of Pt@Co nanostructure, the formation of Pt–Co alloy occurs at the temperature similar to this observed upon

Fig. 4. The evolution of Pt 4f spectra (a, b) and integrated intensities (c, d) of metallic Pt⁰ (red squares), the Pt–Co interface (green circles), the Pt–Co alloy (cyan open circles), and the total Pt 4f signal (black triangles) upon annealing of Pt@Co (a, c) and Co@Pt (b, d) core–shell nanostructures in UHV. The ball models illustrate the morphology of the Pt@Co (a) and Co@Pt (b) core–shell nanostructures on CeO₂(111) before (top) and after annealing to 750 K (bottom). The blue, green, red, and ivory balls represent Pt, Co, O, and Ce atoms, respectively.

annealing of 3 ML Co layer on Pt(111) [43]. In specific, the progressive incorporation of Pt into the Co film was observed above 500 K yielding a homogeneous Pt–Co alloy layer with the stoichiometry close to PtCo [43]. Further annealing of Pt–Co alloy led to a surface enrichment in Pt.

However, according to density functional theory (DFT) calculations [52,53], the chemical ordering in Pt–Co nanoalloys strongly depends on the size and the stoichiometry of the nanoparticles. For instance, in Co-rich nanoparticles, Pt tends to segregate to the surface where it occupies corner and edge sites while terrace sites are mostly occupied by Co. With increasing Pt content, most of the Pt atoms segregate to the surface, although a fraction of Pt atoms was found in the core as well [52]. In Pt-rich nanoparticles, thermodynamically favorable structure forms which consist of a nearly complete Pt-shell followed by subsurface pure Co-shell and Pt–Co alloy at the core. The situation is similar for bigger Co-rich nanostructures (size 4.0 nm), while the stable structure for bigger Pt-rich nanoparticles is slightly different and consists of a Pt-shell followed by a Co-rich Pt–Co alloy subsurface shell, and a Pt-rich Pt–Co alloy core [52].

We assume that in both Pt@Co and Co@Pt nanostructures, the outer shell is Pt-rich while the Pt–Co alloy form subsurface. This assumption is consistent with the decrease of the corresponding Pt–Co alloy contribution with respect to Pt⁰

upon annealing above 600 K.

3.5. Stability of Co@Pt nanostructure with 1 ML Pt-shell in UHV and in O₂

The Co@Pt nanostructure with 1 ML Pt-shell was investigated with respect to the thermal stability in UHV and in O₂ atmosphere. The development of Pt 4f and Co 2p spectra upon annealing of supported Co@Pt in UHV and in the presence of O₂ is shown in Fig. 5.

The top Pt 4f spectrum obtained from the as-prepared Co@Pt nanostructure (Fig. 5a, top) contains two doublet peaks associated with the contributions from Pt–Co interface and metallic Pt⁰. Upon annealing in UHV, the contribution from Pt–Co interface gradually decreases until it vanishes at 600 K. Instead, a new contribution associated with the formation of Pt⁴⁺ emerges at 73.6 eV (Pt 4f_{7/2}) at 700 K. This is accompanied by an additional doublet peak at 75.0 eV (Cu 3p_{3/2}) assigned to a Cu 3p core level signal from the underlying Cu(111) substrate. The emergence of the Cu 3p contribution in the Pt 4f spectra occurs due to thinning and disintegration of CeO₂(111) film upon annealing. The development of the Co 2p spectra (Fig. 5b) is similar to that observed for the Co@Pt nanostructures with a thicker Pt-shell (Section 3.3, Fig. 3c). In particular, the intensity of metallic Co⁰ increases up to 500 K and decreases at

Fig. 5. The evolution of Pt 4f (a, c) and Co 2p (b, d) spectra upon annealing of Co@Pt/CeO₂(111) with 1 ML Pt-shell, in UHV (a, b) and in O₂ (c, d). The ball models illustrate the morphology of Co@Pt core-shell nanostructures supported on CeO₂(111) film. The blue, green, red, and ivory balls represent Pt, Co, O, and Ce atoms, respectively.

higher temperatures (data are not shown). This behavior suggests that the Pt-shell is partially covered by the patches of metallic Co⁰ similarly to the Co@Pt system with thicker Pt-shell (see Section 3.3). Notably, after annealing of the supported Co@Pt nanostructure to 750 K, the Pt 4f spectrum contains a single contribution associated exclusively with metallic Pt⁰. In this respect, the Co@Pt with a 1 ML Pt-shell differs from the Co@Pt with a thicker 1.5 ML Pt-shell as discussed in Section 3.3. The absence of Pt–Co alloy is in line with high stability of 1 ML thick Pt-shell against alloying [47]. Considering the temperature driven Pt enrichment at the surface, we assume that 1 ML Pt-shell in Co@Pt is nearly pure.

The development of Pt 4f and Co 2p spectra upon annealing of the Co@Pt nanostructure with a 1 ML Pt-shell in O₂ is shown in Figs. 5c and 5d, respectively. Following the exposure to O₂ at 110 K, a new component emerged in Pt 4f spectra at 72.7 eV (Pt 4f_{7/2}) due to the formation of a surface platinum oxide associated with the Pt²⁺ state [54]. At the same time, we observed strong oxidation of metallic Co⁰ yielding CoO. The significant increase of the Co²⁺ intensity coupled with the strong attenuation of the Pt 4f intensity suggests that the Co@Pt nanostructure is covered by a layer of CoO. At 550 K, the Pt²⁺ contribution vanished and the Pt⁴⁺ contribution emerged at 550 K at 73.1 eV (Pt 4f_{7/2}). Additionally, a new component

associated with Cu 3*p* emerges at 74.8 eV (Cu 3*p*_{3/2}) at 500 K. The emergence of the strong Cu 3*p* signal is associated with disintegration of CeO₂(111) upon annealing in O₂ above 500 K. With increasing temperature, the intensities of both Pt 4*f* and Co 2*p* spectra decrease significantly while the contribution from Cu 3*p* dominates the spectra. This behavior suggests an encapsulation of the Co@Pt nanostructure by CeO₂ upon annealing in O₂ above 500 K.

3.6. Oxidation and reduction cycles

The oxidation states of Co and Pt in the Co@Pt nanostructures supported on CeO₂(111) were investigated following the subsequent annealing in O₂ and H₂ at different temperatures. The corresponding Pt 4*f* and Co 2*p* spectra obtained from the Co@Pt nanostructures with thin (1 ML) and thick (1.5 ML) Pt-shells are shown in Fig. 6.

In general, we observed that the changes in the Pt 4*f* (Figs. 6a and 6d) and Co 2*p* spectra (Figs. 6b and 6e) were mostly

driven by the oxidation of supported Co@Pt nanostructures upon exposure to O₂. The subsequent annealing in H₂ did not cause any detectable changes in the shapes of Pt 4*f* and Co 2*p* spectra regardless of the thickness of the Pt-shells in the Co@Pt nanostructures. The evolution of the integrated intensities of both metallic Co⁰ and Co²⁺ upon sequential oxidation and reduction of both nanostructures is shown in Figs. 6c and 6f. The progressive oxidation of Co associated with the increase of the Co²⁺ contribution is related to the adsorbate-induced segregation of Co from the core to the surface regardless of the thickness of the Pt-shell in both nanostructures. Interestingly, the intensity of the metallic Co⁰ decreases after the initial exposure to O₂ at 110 K and remains practically constant up to 450 K (1 ML Pt-shell, Fig. 6c) and 500 K (1.5 ML Pt-shell, Fig. 6f). We believe that due to the high surface sensitivity of the Co 2*p* spectra obtained with the photon energy of 930 eV, we were not able to follow the decrease of the metallic Co⁰ in the core. The disappearance of the Co⁰ signal upon annealing at 600 K points to the complete oxidation of metallic Co-core

Fig. 6. The evolution of the Pt 4*f* (a, d) and Co 2*p* (b, e) spectra and the evolution of the integrated metallic Co⁰ and Co²⁺ contributions (c, f) upon subsequent annealing of Co@Pt/CeO₂(111) nanostructures with 1 ML Pt-shell (a–c) and 1.5 ML Pt-shell (d–f) in O₂ (black) and H₂ (green). The top spectra (red) were obtained from as-prepared Co@Pt/CeO₂(111) nanostructures. The ball models demonstrate the morphology of Co@Pt core-shell nanostructures supported on the CeO₂(111) film. The blue, green, red, and ivory balls represent Pt, Co, O, and Ce atoms, respectively.

accompanied by the encapsulation of oxidized Co@Pt nanostructure by a thick layer of CeO₂. We verified complete oxidation of metallic Co-core at 750 K by means of XPS. The onset of the encapsulation is associated with the emergence of the Cu 3p signal above 500 K (Figs. 6a and 6d).

Based on the evolution of the Pt 4f spectra obtained from the Co@Pt nanostructure with 1 ML Pt-shell (Fig. 6a), the decrease of the Pt–Co alloy contribution suggests that, first, the Co from the subsurface alloy is pulled out and oxidized below 300 K in accordance with the observation described in Section 3.4. We assume a similar scenario also in the case of the Co@Pt nanostructure with a 1.5 ML Pt-shell. Above 550 K, the Pt 4f spectra contain only a single contribution associated with Pt⁰ while the contribution from Pt–Co alloy observed earlier under UHV conditions (Fig. 4b) vanishes upon annealing in O₂. This observation suggests the decomposition of the Pt–Co alloy in the supported Co@Pt nanostructure followed by the formation of a surface CoO film. Considering the lack of reduction of CoO upon annealing under H₂, we assume that CoO homogeneously covers the Co@Pt nanostructures regardless of the thickness of the initial Pt-shell. In the resulting morphology, the Pt is buried under a CoO-shell and is not accessible for the activation and dissociation of H₂.

4. Conclusions

Pt@Co and Co@Pt core-shell nanostructures and Co nanoparticles were assembled on well-ordered CeO₂(111) films grown on Cu(111) by means of physical vapor deposition of Co and Pt in UHV. The systems were investigated by means of SRPES and RPES. Below we summarize the most important findings.

(1) Co/CeO₂. The deposition of 0.5 ML of Co onto a CeO₂(111) film at 300 K in UHV leads to the formation of atomically dispersed Co²⁺ ions, coupled with the reduction of Ce⁴⁺ to Ce³⁺. The corresponding process is associated with the formation of Co–CeO₂(111) solid solution. Above 0.5 ML Co, growth of metallic Co nanoparticles was observed. The annealing of 2.5 ML Co revealed the stability region of the metallic Co nanoparticles upon annealing in UHV up to 500 K followed by sintering at higher temperatures.

(2) Pt@Co nanoarchitecture at 300 K. The deposition of 2.5 ML Co onto Pt nanoparticles (size 3 nm) supported on CeO₂(111) film results in the formation of a Pt@Co core-shell nanostructure and Co–CeO₂(111) solid solution. A minor Pt–Co intermixing occurs at the interface between the Pt-core and the Co-shell.

(3) Co@Pt nanoarchitecture at 300 K. The deposition of 1.5 ML Pt onto Co nanoparticles supported on CeO₂(111) film results in the formation of a Co@Pt core-shell nanostructure accompanied by the reduction of Co²⁺ in the Co–CeO₂(111) solid solution due to reactive metal support interaction. A minor Pt–Co intermixing occurs at the interface between Pt-core and Co-shell.

(4) Re-ordering in Pt@Co. Annealing of the Pt@Co nanostructure triggers minor restructuring associated with the formation of the sharp Pt–Co interface. The resulting

nanostructure consists of a Pt-core and a nearly pure Co shell after the annealing to 500 K in UHV. After annealing above 600 K in UHV, the nanostructure consists of a Pt-rich core followed by subsurface Pt–Co alloy shell and a Pt-rich surface shell.

(5) Re-ordering in Co@Pt. Annealing of the Co@Pt nanostructure at 500 K leads to the formation of sharp Pt–Co interface. Additionally, the progressive reduction of Co²⁺ in the Co–CeO₂(111) solid solution yields metallic Co which diffuses onto the Co@Pt nanostructure upon annealing to 500 K. The resulting Co@Pt nanostructure consists of the Co-core and nearly pure Pt-shell which is partially covered by metallic Co in the form of patches, adsorbed Co atoms, or Co inclusions. After the annealing above 600 K in UHV, the nanostructure consists of a Co-rich core followed by subsurface Pt–Co alloy shell and a Pt-rich surface shell.

(6) The effect of the Pt-shell thickness in Co@Pt. The differences caused by the initial thickness of the Pt-shell in supported Co@Pt nanostructures are related to the formation of a subsurface Pt–Co alloy shell upon annealing above 600 K. For thin Pt-shells (1 ML), the subsurface Pt–Co alloy shell is not formed in the Co@Pt upon annealing in UHV.

(7) The oxidation of Co@Pt with a thin Pt-shell (1 ML). The exposure of Co@Pt nanostructure (1 ML of Pt) to O₂ at different temperatures leads to the formation of surface PtO coupled with the oxidation of subsurface Co to CoO between 110 and 500 K. Above 500 K, the CoO grows at the expense of the Co-core which is accompanied by the disintegration of the CeO₂ substrate and encapsulation of oxidized Co@Pt nanostructure by a CeO₂ film. The resulting structure at 500 K most likely consists of Co-core followed by Pt-shell followed by CoO-shell. This nanostructure is encapsulated by a CeO₂ film above 500 K.

(8) Oxidation/reduction cycles with Co@Pt. The structural changes in the Co@Pt nanostructures with 1 ML and 1.5 ML Pt-shells during sequential exposure to O₂ and H₂ at different temperatures are primarily driven by the oxidation. The exposure of oxidized Co@Pt nanostructures to H₂ has no effect on the shape of the Pt 4f and Co 2p spectra regardless of the thickness of the Pt-shell. Notably, we observed decomposition of subsurface Pt–Co alloy due to oxidation of Co in the Co@Pt nanostructure. The resulting nanostructures under the oxidation/reduction cycles show strong similarities regardless of the thickness of the Pt-shell. In all cases, the Pt-shells are covered by a CoO layer and are eventually encapsulated by a CeO₂ film above 500 K.

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Graphical Abstract

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Nanoscale architecture of ceria-based model catalysts: Pt–Co nanostructures on well-ordered CeO₂(111) thin films

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The chemical composition and atomic ordering in the model Co@Pt core-shell nanostructure and in the CeO₂(111) support are functions of temperature. The most important changes are associated with the formation of subsurface Pt–Co alloy.

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钨基模型催化剂的纳米结构：有序CeO₂(111)薄膜上的Pt-Co纳米颗粒

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摘要: 制备并表征了原子分散的模型体系: 氧化钨负载的Pt-Co核壳催化剂. 采用超高真空物理气相沉积法制备了有序CeO₂(111)膜上的Pt@Co和Co@Pt核壳纳米结构, 并用同步辐射光电子能谱和共振光发射光谱对其进行了研究. 在低Co覆盖率(0.5 ML)下Co在CeO₂(111)上沉积生成Co-CeO₂(111)固溶体, 然后在更高Co覆盖率下生长为金属Co纳米粒子. Pt@Co和Co@Pt两种模型结构在300–500 K温度范围内都能稳定地抗烧结. 在500 K退火后, Pt@Co纳米结构含有接近纯的钨壳, 而Co@Pt中的钨壳部分被金属钨覆盖. 在550 K以上, 在Pt@Co和Co@Pt纳米结构中近表面区域的重新排序中产生了次表层的Pt-Co合金和富钨外壳. 对于Co@Pt纳米粒子, 近表面区域的化学有序性取决于沉积钨壳的初始厚度. 无论初始钨壳的厚度如何, 在有氧存在下对Co@Pt纳米结构进行退火, 都会导致Pt-Co合金的分解以及Co的氧化. Co的逐步氧化与吸附质诱导的Co偏析共同导致在负载的Co@Pt纳米结构表面形成厚的CoO层. 这一过程伴随着CeO₂(111)薄膜的裂解, 以及在550 K以上氧气中退火后CeO₂包裹氧化的Co@Pt纳米结构. 很明显, 于不同温度下在氧气和氢气的氧化-还原循环过程中, 无论钨的初始厚度是多少, 负载的Co@Pt纳米颗粒的结构和化学成分的变化主要是由氧化所致, 而还原处理的影响则很小.

关键词: 核壳纳米粒子; 模型催化剂; Pt-Co; 氧化钨; 化学有序性; 同步辐射光电子能谱

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