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Article

Interface-controlled synthesis of CeO₂(111) and CeO₂(100) and their structural transition on Pt(111)

Yi Zhang ^{a,c}, Wei Feng ^b, Fan Yang ^{a,*}, Xinhe Bao ^{a,#}^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China^b Science and Technology on Surface Physics and Chemistry Laboratory, Jiangyou 621908, Sichuan, China^c University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Ceria-based catalytic materials are known for their crystal-face-dependent catalytic properties. To obtain a molecular-level understanding of their surface chemistry, controlled synthesis of ceria with well-defined surface structures is required. We have thus studied the growth of CeO_x nanostructures (NSs) and thin films on Pt(111). The strong metal-oxide interaction has often been invoked to explain catalytic processes over the Pt/CeO_x catalysts. However, the Pt-CeO_x interaction has not been understood at the atomic level. We show here that the interfacial interaction between Pt and ceria could indeed affect the surface structures of ceria, which could subsequently determine their catalytic chemistry. While ceria on Pt(111) typically exposes the CeO₂(111) surface, we found that the structures of ceria layers with a thickness of three layers or less are highly dynamic and dependent on the annealing temperatures, owing to the electronic interaction between Pt and CeO_x. A two-step kinetically limited growth procedure was used to prepare the ceria film that fully covers the Pt(111) substrate. For a ceria film of ~3–4 monolayer (ML) thickness on Pt(111), annealing in ultrahigh vacuum (UHV) at 1000 K results in a surface of CeO₂(100), stabilized by a c-Ce₂O₃(100) buffer layer. Further oxidation at 900 K transforms the surface of the CeO₂(100) thin film into a hexagonal CeO₂(111) surface.

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1. Introduction

The controlled synthesis of oxide materials exposing only desired facets has been of general interest in the fields of solid state chemistry, material science, and heterogeneous catalysis [1,2]. Cerium oxides, as the most abundant rare earth materials, have triggered tremendous interest in heterogeneous catalysis in particular, because of their unique capability to store and release oxygen and to facilitate switch between Ce⁴⁺ and Ce³⁺

oxidation states [3–6]. As ceria-based materials are increasingly exploited for catalytic applications, molecular-level understanding of the surface chemistry of ceria has become an urgent issue.

Conventionally, single crystals of ceria cut out from the minerals have been used as models for surface chemistry and catalysis studies [7–10]. However, recent studies [11,12] have pointed to the influence of impurities in ceria single crystals, mainly fluorine, which could cause misinterpretation of the

^{*} Corresponding author. Tel: +86-411-84379765; Fax: +86-411-84694447; E-mail: fyang@dicp.ac.cn[#] Corresponding author. Tel: +86-411-84686637; Fax: +86-411-84694447; E-mail: xhbao@dicp.ac.cn

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surface chemistry of ceria. Meanwhile, the growth of ceria thin films on planar metal or oxide surfaces offers the advantage of high crystalline quality and purity, and has been used as an alternative method to synthesize model systems for catalytic studies [13–19]. Particularly, the growth of ceria on metal surfaces could be used to prepare (1) sub-monolayer (ML) ceria nanostructures (NSs) that allow the study of the metal-oxide interface [20–23], or (2) ceria thin films exhibiting different surface structures tuned by the interfacial interaction [24–26]. Thus, the versatility of oxide growth on metal single crystals has made it an attractive approach for the preparation of model catalytic systems. However, the growth of ceria thin films exposing high-surface-energy facets has been challenging [27].

Among the low-index facets of ceria, the surface structure of $\text{CeO}_2(100)$ has been the least definitive and its catalytic chemistry has thus remained most puzzling [27]. As a polar surface, $\text{CeO}_2(100)$ is expected to be highly active for catalytic reactions [28]. However, in practice, ceria nanocubes, which dominantly expose the (100) facets, have also not been found to be as active as ceria polyhedra, which expose mainly the (111) facets [29,30]. To elucidate the surface chemistry of $\text{CeO}_2(100)$, model $\text{CeO}_2(100)$ catalysts with well-defined surface structures have been highly desired but are not easy to achieve on metal surfaces. Although there have been a few studies reporting the growth of $\text{CeO}_2(100)$ nanoparticles on $\text{Ru}(0001)$ [31,32] and the pre-oxidized surface of $\text{Cu}(111)$ [33–35], their surface atomic structures and the origin of formation have not been clear. Moreover, the growth of $\text{CeO}_2(100)$ thin films remains to be explored.

Here, we report the growth of well-defined $\text{CeO}_2(111)$ and $\text{CeO}_2(100)$ on $\text{Pt}(111)$ and demonstrate that the interfacial interaction between Pt and ceria could be utilized to selectively synthesize $\text{CeO}_2(111)$ or $\text{CeO}_2(100)$ thin films. The Pt/CeO_x system has been widely used for catalytic reactions, including CO oxidation [36], the water-gas-shift reaction [4], and the steam reforming reaction [37]. A strong metal-oxide interaction between Pt and ceria [38] has been observed to influence or determine the catalytic performance of Pt/CeO_x catalysts. However, the strong interaction between Pt and ceria has not been well-understood. Particularly, how the interfacial interaction could affect the structure of supported oxides remains largely unexplored. We have thus studied the growth and structures of CeO_x NSs and ultrathin films on $\text{Pt}(111)$ to understand the nature of the strong metal-oxide interaction in the Pt/CeO_x system.

2. Experimental

The experiment was carried out in a combined UHV system. The scanning tunneling microscope (STM) chamber is equipped with a Createc low-temperature scanning tunneling microscope (LT-STM, base pressure $< 4 \times 10^{-11}$ mbar). The preparation chamber is equipped with an X-ray photoelectron spectroscopy (XPS), cleaning facilities, and an e-beam evaporator (base pressure $< 5 \times 10^{-11}$ mbar). STM measurements were conducted at 78 K, with an electrochemically etched tungsten tip. STM images were processed with SPIP software from Im-

age Metrology, Denmark. XPS spectra were recorded with a SPECS PHOIBOS 100 analyzer using an $\text{Al } K_{\alpha}$ X-ray source ($h\nu = 1486.6$ eV) and a $\text{Mg } K_{\alpha}$ X-ray source ($h\nu = 1253.6$ eV) at the normal emission angle.

The $\text{Pt}(111)$ single crystal (MaTeck) was cleaned by cycles of 1.5 keV Ar^+ ion sputtering and annealing at 1000 K. Ce atoms were evaporated from a Ce foil (Alfa Assar, $> 99.95\%$) in the e-beam evaporator and the evaporation flux was monitored by a grid at the exit of the evaporator. CeO_x NSs or thin films were prepared on $\text{Pt}(111)$ by evaporating Ce atoms in 10^{-7} mbar O_2 at 600 K. The deposition rate of ceria was calibrated by STM measurements on the surface coverages of CeO_x NSs and layers. Because as-deposited CeO_x NSs and layers could appear in the form of multilayers, monolayer equivalent (MLE) was used to represent the surface coverage, which was determined from the STM-measured surface area times the layer number of CeO_x NSs or layers. To prepare a ceria thin film that fully covers the metal substrate, a kinetically limited growth process was employed, i.e., the growth of the interfacial layers of ceria at 200 K, which was followed by the deposition of ceria at 600 K.

3. Results and discussion

3.1. Growth of $\text{CeO}_2(111)$ on $\text{Pt}(111)$ from nanostructures to films

Fig. 1a shows a 0.4 MLE $\text{CeO}_x/\text{Pt}(111)$ prepared by evaporating Ce atoms in 1.3×10^{-7} mbar O_2 at 600 K. As-grown CeO_x NSs are found both at the step edges and on the terraces of $\text{Pt}(111)$ and exhibit sizes ranging from 2 nm to 10 nm. These

Fig. 1. STM images on the morphology and structures of 0.4 MLE CeO_x NSs on $\text{Pt}(111)$. (a) 0.4 MLE CeO_x NSs on $\text{Pt}(111)$ prepared by evaporating Ce atoms in 1.3×10^{-7} mbar O_2 at 600 K. As-grown CeO_x NSs show three types of structures (marked by three squares) with three different apparent heights. High-resolution STM images of these three types of structures: (b) type-I ML CeO_x NS, (c) type-II ML CeO_x NS, and (d) BL CeO_x NS. Scanning parameters: (b–d) sample bias (V_s) = -1.0 V, tunneling current (I_t) = 0.12 nA.

CeO_x NSs consist of both monolayer (ML) and bilayer (BL) oxide islands. For ML CeO_x NSs, two types of ceria islands are observed, with type-I exhibiting the ordered crystalline structure and type-II displaying irregular shape and surface structure (Fig. 1b and 1c). Type-I ML CeO_x NSs predominantly exhibit the hexagonal shape with diameter < 5 nm. Their surfaces display the hexagonal CeO₂(111) lattice, with a lattice spacing of 3.8 Å (Fig. 1b). In contrast, type-II ML CeO_x NSs are more popular on and usually appear larger than type-I ML CeO_x NSs on Pt(111). The apparent height of type-II ML CeO_x NSs (~2.9 Å) is lower than that of type-I ML CeO_x NSs (~3.3 Å). Thus, type-II ML CeO_x NSs can be assigned as sub-stoichiometric CeO_x NSs, while type-I ML CeO_x NSs expose a stoichiometric CeO₂ surface. Meanwhile, BL CeO_x NSs have an apparent height (~6.0 Å) approximately twice that of ML CeO_x NSs and display mostly the hexagonal shape. The surfaces of BL CeO_x NSs always show the hexagonal CeO₂(111) lattice, with a lattice spacing of 3.8 Å (Fig. 1d).

When the surface coverage of ceria increases, CeO_x NSs start to coalesce with each other (Fig. 2a). Both ML and BL CeO_x NSs can still be observed on the surface. ML CeO_x NSs usually appear sub-stoichiometric, i.e., in the form of type-II CeO_x NSs. While type-I ML CeO_x NSs retain the truncated triangle shape with ordered CeO₂(111) lattice (Fig. 2b), type-II ML CeO_x NSs appear more ordered than in Fig. 1 and display straight step edges. Bright protrusion lines can also be observed on the surface of type-II ML CeO_x NSs (Fig. 2c), whereas the apparent height and the atomic lattice suggest these CeO_x NSs are sub-stoichiometric. Meanwhile, the shape of BL CeO_x NSs becomes more triangular (Fig. 2d).

Compared to Fig. 1, the growth of 0.8 MLE CeO_x NSs on

Pt(111) led to ML and BL CeO_x NSs with a more triangle-like shape, which could be understood by the preferred growth of CeO_x. When deposited, cerium atoms would likely diffuse in the form of cerium oxide clusters on Pt(111) and attach to the step edges of existing CeO_x NSs. As a hexagonal ML CeO_x NS usually exposes two types of <110>-oriented edge structures alternating along the steps (Fig. 2e), we found that type-A edges are usually longer than type-B edges, in consistence with a previous report [39]. During growth, type-A edges might exhibit a lower barrier for the attachment of cerium oxide clusters, which causes the asymmetric growth of CeO_x NS and eventually the formation of triangle-like CeO_x NSs. The hexagonal BL CeO_x NSs also feature two types of edge structures, i.e., <100>-oriented edge and <111>-oriented edge [40]. Apparently, the <111>-oriented edges are more thermodynamically stable and thus favored during the growth of BL CeO_x NSs, leading to the formation of a triangular shape.

When the surface of the sample in Fig. 2a was annealed to 800 K in UHV, the morphology of CeO_x NSs changed drastically (Fig. 2f). ML CeO_x NSs disappeared and all CeO_x NSs became BL CeO_x NSs, indicating that BL CeO_x NSs are more thermodynamically stable. This also implied that the interaction between ceria layers is stronger than the interaction between ceria and Pt(111). Since the surface of BL CeO_x NSs always exhibits the stoichiometric CeO₂(111) lattice (Fig. 2g), the interfacial ceria layer of BL CeO_x NSs is expected to be sub-stoichiometric upon the transformation from ML to BL CeO_x NSs, which is further supported by the Ce 3d spectra from XPS measurements (Fig. 2h). Note that, after annealing at 800 K, the CeO_x NSs become hexagonal, indicating that the two types of step edges exhibit a similar stability in UHV.

Fig. 2. The morphology and structures of 0.8 MLE CeO_x NSs on Pt(111). (a) Large-scale STM image of 0.8 MLE CeO_x NSs, where both ML and BL CeO_x islands appear triangle-like. High-resolution STM images of (b) type-I ML CeO_x NS, (c) type-II ML CeO_x NS, and (d) BL CeO_x NS. (e) Hexagonal ML CeO_x NS exposes two types of <110>-oriented edges that have opposite descents. Pt atoms, Ce atoms, surface and subsurface O atoms are displayed in gray, white, red, and brown, respectively. (f) STM image of the surface of the sample in (a) after annealing in UHV at 800 K for 10 min. ML CeO_x NSs were found to transform into BL CeO_x NSs. (g) High-resolution STM image of the BL CeO_x NS marked in (f). (h) Ce 3d XPS spectra of the 0.8 MLE sample after the annealing in UHV at 800 K for 10 min. Scanning parameters: (b,d) $V_s = -1.0$ V, $I_t = 0.11$ nA; (c) $V_s = 1.6$ V, $I_t = 0.04$ nA; (g) $V_s = 0.6$ V, $I_t = 0.10$ nA.

Fig. 3. The morphology and structures of 1.6 MLE CeO_x NSs on Pt(111). (a) STM image of 1.6 MLE $\text{CeO}_x/\text{Pt}(111)$ surface after annealing in UHV at 850 K for 10 min, which displays dominantly BL and TL CeO_x NSs. Atomic-resolution STM image of BL and TL CeO_x NSs are displayed in (b) and (c), respectively. The squared area in (a) is enlarged in (d), which shows small CeO_x clusters in the size between 1 nm and 5 nm on the surface terrace of TL CeO_x NSs. (e) Atomic-resolution STM image of these supported CeO_x clusters, showing the $\text{CeO}_2(111)$ lattice. (f) Structural model of the supported CeO_x cluster. For the ceria substrate, Ce and O atoms are displayed in white and pink, respectively. For CeO_x cluster, Ce atoms, surface and sub-surface O atoms are displayed in blue red, and gold, respectively. Scanning parameters: (b) $V_s = 1.0$ V, $I_t = 0.10$ nA; (c) $V_s = 1.5$ V, $I_t = 0.11$ nA; (e) $V_s = 1.2$ V, $I_t = 0.29$ nA.

As for the surface of 1.6 MLE $\text{CeO}_x/\text{Pt}(111)$, the annealing at 850 K in UHV resulted in the Pt surface being covered by CeO_x NSs with straight step edges and of BL or tri-layer (TL) thickness (Fig. 3a). The atomic-resolution STM image of the BL CeO_x NSs reveals a $(3 \times 3)\text{-CeO}_2(111)$ super-lattice (Fig. 3b), which has been regularly observed in the growth of ceria on Pt(111).

The (3×3) super-structure of $\text{CeO}_2(111)$ can be ascribed to the formation of a coincidence lattice, i.e., the $(3 \times 3)\text{-CeO}_2(111)$ lattice in coincidence with the $(4 \times 4)\text{-Pt}(111)$ lattice. On the surface of TL CeO_x NSs, the (3×3) super-structure of $\text{CeO}_2(111)$ is less obvious, but the electronic modulation by the Pt substrate can still be observed (Fig. 3c).

Interestingly, there are also numerous small CeO_x clusters on top of TL CeO_x NSs, but not on BL CeO_x NSs, even after annealing at 850 K (Fig. 3d). These CeO_x clusters typically exhibit a size ranging from 1.5 nm to 5 nm. Atomic-resolution STM images of these supported CeO_x clusters show that their surfaces expose the hexagonal $\text{CeO}_2(111)$ lattice (Fig. 3e). Note that, ML-, BL- and TL- CeO_x NSs below 5 nm in size are usually not stable on Pt(111) after annealing at 850 K, and coalesce to form larger NSs. The presence of these small and crystalline CeO_x clusters indeed suggests a much stronger interlayer interaction for ceria NSs above TL thickness. The electronic interaction between Pt(111) and ceria could strongly affect the diffusivity and stability of supported CeO_x clusters. However, when the layer thickness of CeO_x NSs exceeds the TL thickness, electron transfer from Pt becomes rather weak, thereby exerting a negligible effect on the diffusion of top-layer CeO_x clusters.

From the above, although ceria NSs tend to wet the Pt(111) surface much better than the Au(111) substrate [41,42], the growth of ceria NSs on Pt(111) does not follow exactly the layer-by-layer mode. Rather, the Pt(111) surface remains partially uncovered when Ce is deposited onto Pt(111) at elevated temperatures in the O_2 atmosphere. Even for 2 MLE ceria deposition at 600 K, which was followed by annealing at 800 K in 4×10^{-7} mbar O_2 , pits with a depth of ~ 0.6 nm (BL thickness) can be easily observed on the surface of ceria thin films on Pt(111) (Fig. 4a–4c). Moreover, when an additional ~ 2 MLE

Fig. 4. The morphology of CeO_x layers grown on Pt(111) at 600 K. (a,b) STM images of 2 MLE CeO_x layers grown by depositing Ce atoms in 1×10^{-7} mbar O_2 at 600 K, which was followed by annealing at 800 K in 4×10^{-7} mbar O_2 for 15 min. The line profile in (b) is displayed in (c). (d,e) STM images of the surface of the sample in (a) after the additional deposition of 2 MLE Ce atoms in 1×10^{-7} mbar O_2 at 600 K, which was followed by annealing at 900 K in 1×10^{-7} mbar O_2 for 12 min. The line profile in (e) is displayed in (f).

ceria was deposited at 600 K, the Pt(111) surface is still not fully covered, as evidenced by the number of pits with a depth of ~ 1.2 nm on the ceria surface (Fig. 4d–4f). Thus, even the deposition of 4 MLE ceria films cannot fully cover the Pt(111) substrate. This could be attributed to the much stronger interaction between ceria layers than between ceria and Pt(111).

To synthesize a well-defined ceria film that fully covers the Pt(111) substrate, a kinetically limited growth procedure was employed [13]. First, Ce atoms were deposited onto Pt(111) at 200 K in 1×10^{-7} mbar O_2 . After deposition, the Pt(111) surface was covered by small CeO_x clusters, which dispersed homogeneously on the surface and formed nucleation centers for further growth of ceria films on Pt(111) (Fig. 5a and 5b). Then, Ce atoms were deposited onto Pt(111) at 600 K in 1×10^{-7} mbar O_2 . The as-grown ceria films were further annealed to 900 K in 2×10^{-7} mbar O_2 to improve the crystalline quality. This procedure could lead to the formation of a well-ordered $CeO_2(111)$ film, covering fully the Pt(111) surface (Fig. 5c and 5d). On the surface of the flat $CeO_2(111)$ film, both surface and sub-surface O vacancies can be observed, while the (3×3) super-structure of $CeO_2(111)$ is not visible in the STM image (Fig. 5e), indicating that electronic transfer from the Pt(111) substrate imposes little effect on the surface of $CeO_2(111)$ with thickness above four layers. Meanwhile, Ce 3d spectra from XPS measurements show that the $CeO_2(111)$ thin film is indeed dominated by Ce^{4+} ions on the film surface (Fig. 5f).

3.2. Growth and structure of $CeO_2(100)$ on Pt(111)

In Section 3.1, we have shown that the first three layers of ceria could be affected by electronic interaction with the

Pt(111) substrate. Using the kinetically limited growth procedure described above, a 3.5 MLE ceria thin film was deposited on Pt(111). Instead of annealing in O_2 at 900 K, the ceria film was annealed in UHV at 1000 K, which also resulted in the ceria film that fully covers the Pt(111) substrate. Surprisingly, a drastic change was observed in the morphology of the ceria film (Fig. 6a and 6b). Rather than displaying the hexagonal surface lattice of $CeO_2(111)$, the surface of UHV-annealed ceria film exhibits square or rectangular lattices, which can also be inferred from the shape of the ceria islands. The rectangular ceria islands are typically 10–60 nm in diameter. XPS measurements show that UHV annealing at 1000 K causes significant reduction of the ceria film, such that Ce 3d spectra (Fig. 6c) show the surface to be highly reduced and dominated by Ce^{3+} ions. Thus, the symmetry change of the surface lattice is caused by the reduction of the ceria film. The reduction process is facilitated by the strong metal-oxide interaction between cerium oxide and Pt(111), consistent with the findings from CeO_2 -on-Ag catalysts. Chang et al. [43] have reported surface-enhanced Raman spectroscopy (SERS) and catalytic studies of ceria thin layers on Ag particles and showed that Ce(III) species could be stabilized by the Ag- CeO_2 interaction.

At the lower layer of the film surface (Fig. 7a), which corresponds to the ceria thin film of TL thickness, an ordered square lattice structure can be easily observed on the film surface. The atomic structure of the square lattice is magnified in Fig. 7a, and shows a lattice spacing of ~ 1.1 nm, which can thus be attributed to the reconstruction of a (100) surface. Three rotational domains with such a square lattice can be identified on the surface of the TL ceria film, and exhibit a rotational angle of 120° against each other. Previous studies have explored the

Fig. 5. The morphology of CeO_x layers grown on Pt(111) by a kinetically limited growth process. The growth process includes two steps: (1) the growth of interfacial ceria layers at 200 K in 1×10^{-7} mbar O_2 , which resulted in the surface depicted by STM images in (a) and (b); (2) the subsequent growth of ceria layers by depositing Ce atoms at 600 K in 1×10^{-7} mbar O_2 . The as-grown surface was then annealed at 900 K in 2×10^{-7} mbar O_2 for 20 min, which resulted in the CeO_x thin films fully covering the Pt substrate. The surface morphology of the annealed CeO_x thin films is depicted by STM images in (c) and (d). (e) Atomic-resolution STM image and (f) Ce 3d XPS spectra suggest the annealed CeO_x thin films display a well-defined $CeO_2(111)$ surface. Scanning parameters: (e) $V_s = 3.0$ V, $I_t = 3.6$ nA.

Fig. 6. The morphology of 3.5 MLE CeO_x on Pt(111) after the UHV annealing at 1000 K. (a,b) STM images of a 3.5 MLE CeO_x /Pt(111) surface. CeO_x was deposited on Pt(111) by the two-step kinetically limited growth progress. Instead of annealing the as-deposited CeO_x surface in O_2 , the surface was annealed in UHV at 1000 K, resulting in the CeO_x thin films fully covering the Pt substrate. Rectangle-shaped CeO_x islands could be observed on the CeO_x film surface. (c) Ce 3d XPS spectra on the surface of the sample in (a), indicating that the CeO_x film surface was highly reduced.

Fig. 7. Surface structure of the c- $\text{Ce}_2\text{O}_3(100)$ buffer layer on Pt(111). (a) Atomic-resolution STM image on the surface of the third CeO_x layer, showing a square surface lattice with the lattice spacing of ~ 1.1 nm. Three different rotational domains of the square lattice structure could be observed in (a), with white lines marking the major running directions of these CeO_x domains. The surface structure of the CeO_x layer observed in (a) could be assigned to c- $\text{Ce}_2\text{O}_3(100)$ and its structural model is shown in (b). Ce and O atoms are displayed in white and red, respectively. (c) The structural model showing Ce atoms in the (4×4) structure of c- $\text{Ce}_2\text{O}_3(100)$ could form a coincidence lattice with Pt(111). Ce and Pt atoms are displayed in blue and gray respectively. Scanning parameters: (a) $V_s = 3.0$ V, $I_t = 0.02$ nA.

$\text{CeO}_2 \leftrightarrow \text{Ce}_2\text{O}_3$ transition of the CeO_2 (100) phase on Cu(111) induced by the deposition of Ce atoms [35]. The initial Ce deposition can cause surface reconstruction, to transform $p(2 \times 2)\text{-CeO}_2(100)$ into $(1 \times 1)\text{-CeO}_2(100)$. Low-energy electron diffraction (LEED) patterns show that further deposition of Ce atoms can lead to a surface reduction to form a $c(4 \times 4)$ structure, which is attributed to the c- $\text{Ce}_2\text{O}_3(100)$ phase. Likewise, the observed square lattice in Fig. 7a can be assigned as c- $\text{Ce}_2\text{O}_3(100)$.

The symmetry of thin oxide films grown on planar metal surfaces was usually dictated by the symmetry of the metal substrate. That being said, the growth of ceria on the (111) surface of metals should result in the $\text{CeO}_2(111)$ surface, as described in Section 3.1. However, with careful control of the growth parameters, the (100) surface of cerium oxide could also be synthesized on the (111) surface of metal single crystals. Yang et al. [33] have shown that $\text{CeO}_2(100)$ could be grown on Cu(111) by pre-oxidizing the Cu(111) substrate to form a surface oxide with rectangular symmetry. Flege et al. [32] showed that the growth of ceria at 830 °C or above on Ru(0001) could result in rectangular ceria nanoparticles owing to the formation of a coincidence lattice at the oxide–substrate interface. Höcker et al. [26] showed also that ceria nanoparticles on Ru(0001) could be reduced from $\text{CeO}_2(111)$ to cubic

$\text{Ce}_2\text{O}_3(111)$ at 700 °C in UHV.

In this study, we showed that the surface symmetry of ceria could be altered simply by its reduction at 1000 K. The electronic interaction between ceria layers and Pt(111) could facilitate the reduction of ceria significantly to induce the formation of Ce_2O_3 . Meanwhile, the Pt(111) substrate also provides an excellent substrate to form a coincidence lattice with c- $\text{Ce}_2\text{O}_3(100)$, which is briefly illustrated in Fig. 7c. The near-perfect matching provides an explanation for the observation of c- $\text{Ce}_2\text{O}_3(100)$, indicating that the Pt(111) substrate not only facilitates the reduction of cerium oxide via electron transfer but also provides a proper template to stabilize the highly reduced Ce_2O_3 phase.

The top layer (the fourth layer) of the ceria film after UHV annealing exhibits a row-like $(3 \times n)$ surface structure (Fig. 8a). The atomic-resolution STM image (Fig. 8b) shows that the surface has a square lattice with a lattice spacing of ~ 3.9 Å, which corresponds to the surface lattice of $\text{CeO}_2(100)$. Nörenberg et al. [44] have studied the surface structures of $\text{CeO}_2(100)$ single crystals using STM and LEED. After annealing to 900 °C, the $\text{CeO}_2(100)$ surface exhibited the (3×1) and (3×2) reconstruction, which shows a similar structure to the $(3 \times n)$ rows observed in our study. Thus, the $(3 \times n)$ reconstruction observed on the ceria film on Pt(111) could be attributed to the surface

Fig. 8. Surface structures of the $\text{CeO}_2(100)$ layer and NSs on Pt(111). (a) Large-scale and (b) atomic-resolution STM images on the fourth CeO_x layer showing a (3×1) reconstruction of the $\text{CeO}_2(100)$ surface. The (3×1) reconstruction appears as bright rows in (b). (c) Atomic-resolution STM image of the CeO_2 island on the fourth CeO_x layer in (a) shows the (1×1) - $\text{CeO}_2(100)$ surface. (d) The structural model of the (1×1) - $\text{CeO}_2(100)$ surface. Ce and O atoms are displayed in white and red, respectively. Atomic-resolution STM images of surface and sub-surface oxygen vacancies are displayed in (g) and (h), respectively. Scanning parameters: (a,c) $V_s = 2.0$ V, $I_t = 0.12$ nA; (b) $V_s = 2.0$ V, $I_t = 0.13$ nA; (e,f) $V_s = 2.0$ V, $I_t = 0.11$ nA.

reconstruction of $\text{CeO}_2(100)$, which lowers the charge accumulation on the polar surface of $\text{CeO}_2(100)$. In addition, bubble-like square protrusions could also be observed on the surface of the fourth ceria layer and appear ~ 0.6 Å higher than the neighboring surface plane. These protrusions display the same $\text{CeO}_2(100)$ lattice as that of the neighboring surface plane. The height of these protrusions could be due to the inhomogeneity of the ceria layer underneath, which could be inferred from the morphology of the uncovered TL ceria film. Point defects could also be found on the top-layer surface of ceria and as dark holes in the square lattice, which could be attributed to a missing O atom (Fig. 8b).

On top of the ceria film surface, there were also ceria nanoislands, as illustrated in the lower part of Fig. 8a. The surface structure of ceria nanoislands is the same as the top layer (the fourth layer) of the ceria film. However, no (3×1) modulation is observed on the surfaces of ceria islands (Fig. 8c). Rather, these islands exhibit the (1×1) - $\text{CeO}_2(100)$ surface lattice. Similar to the growth of $\text{CeO}_2(111)$ thin films on Pt(111), the thicker the ceria film is, the less electronic modulation that surface ceria layer receives. Density functional theory (DFT) calculations have proposed a structural model for the reconstructed surface of $\text{CeO}_2(100)$, that could compensate for the extra charge of the polar (100) surface while preserving the primitive (1×1) cell [45]. Fig. 8d shows that, by removing half of the outermost O^{2-} ions, the surface polarity could be compensated and the remaining O^{2-} ions could be arranged in a check-board-like pattern, such that the surface remains a (1×1) structure. This polar-compensated (100) structure has also been confirmed by an angle-resolved mass spectroscopy study on the $\text{CeO}_2(100)$ film [46]. Note that, previous studies on the growth of $\text{CeO}_2(100)$ NSs on metal substrates have not been

able to synthesize $\text{CeO}_2(100)$ with a (1×1) structure. Our study suggested that the formation of a c- $\text{Ce}_2\text{O}_3(100)$ buffer layer could serve as a template for the overlayer growth of the $\text{CeO}_2(100)$ film and NSs.

On ceria nanoislands, two types of vacancy sites could be identified. Fig. 8e shows a missing atom in the square lattice, which is most likely a surface oxygen vacancy. In contrast, Fig. 8f shows the surface character of a sub-surface vacancy or vacancies, which appear as a cross-like dark area, and no missing atoms can be observed in the surface lattice.

When the (100) surface of the ceria film was annealed further at 900 K in 2×10^{-7} mbar O_2 , the squared-shaped islands disappeared, along with the squared surface lattice of $\text{CeO}_2(100)$. The ceria film transformed again into the $\text{CeO}_2(111)$ surface (Fig. 9a). The hexagonal surface lattice of $\text{CeO}_2(111)$ could be clearly resolved by the atomic-resolution STM image in Fig. 9b. Note that, the ceria thin film of TL thickness on Pt(111) and exhibiting the $\text{CeO}_2(111)$ surface structure could be transformed into the $\text{CeO}_2(100)$ surface by annealing the film in UHV. However, such a transformation cannot be observed on thicker ceria films. Once the $\text{CeO}_2(111)$ thin film of four-layer thickness is formed, high-temperature annealing or reduction cannot reverse the structure of $\text{CeO}_2(111)$ back to $\text{CeO}_2(100)$. This is consistent with the growth study observation in Section 3.1 that the fourth layer of $\text{CeO}_2(111)$ is not or much less affected by the electronic interaction with the Pt(111) substrate, and thus much less flexible than thinner ceria layers on Pt(111).

While the strong metal-support interaction (SMSI) has often been invoked to explain their unique catalytic properties, the structural dynamics demonstrated above could provide an atomic-scale understanding of catalysis over ceria-supported Pt group metal catalysts. For instance, during the activation of three-way catalysts in a reducing atmosphere, Golunski *et al.* [47] have observed the migration of partially reduced ceria layers over the surface of Pt particles, which led to the loss of metal surface areas, but could still enhance the three-way catalytic activities of Pt/ CeO_2 catalysts, even at low temperatures. While SMSI has been suggested to promote the formation of oxygen vacancies on ceria, we provided atomic-level evidence for the formation of interfacial Ce_2O_3 layer upon reduction, which could be responsible for the enhanced activities of

Fig. 9. The morphology of 3.5 MLE CeO_x on Pt(111) after the annealing at 900 K in O_2 . (a,b) After annealing the surface of the sample in Fig. 6 at 900 K in 2×10^{-7} mbar O_2 , the morphology completely changed, and the surface returned to hexagonal $\text{CeO}_2(111)$ surface. Scanning parameters: (b) $V_s = 3.0$ V, $I_t = 1.0$ nA.

Pt/CeO₂ catalysts [48]. Indeed, Pt nanoparticles with ceria layers have been employed in catalyst synthesis in recent practices and shown remarkable activities for CO oxidation [49] and the water-gas shift reaction [50]. Similar enhancement by ceria overlayers could also be observed on other metal particles, such as Pd [51], Ag [43], and Ir [52]. Thus, our observation of the structural dynamics of ceria thin layers on Pt(111) could be of general relevance to the catalytic interface formed between precious metals and ceria, and provide a profound understanding of the metal-oxide interfacial interaction.

4. Conclusions

We studied the growth and structures of CeO_x NSs and thin films on Pt(111). At low ceria coverage (0.4 MLE), both ML and BL CeO_x NSs were present on the Pt surface upon the deposition of ceria at 600 K. Two types of ML CeO_x NSs were found on Pt(111), with one type showing an ordered and stoichiometric surface of CeO₂(111) and the other appearing sub-stoichiometric with a disordered surface structure. An increase in the surface coverage of ceria induces a change in the shape of CeO_x NSs into a triangle-like shape and the formation of TL CeO_x NSs. After annealing at 800 K, ML CeO_x NSs transform into the more stable form of BL CeO_x NSs. Both BL and TL CeO_x NSs show that the stoichiometric surface of CeO₂(111) and their interfacial CeO_x layers were easily reduced due to the electronic interaction with the Pt substrate. Small CeO_x clusters supported on TL CeO_x NSs could be observed on the 1.6 MLE CeO_x/Pt(111) surface. These CeO_x clusters also displayed the surface lattice of CeO₂(111) and exhibited a thermal stability much more superior than that of ML, BL or TL CeO_x NSs of similar size on Pt(111). This implied that the electronic interaction with the Pt substrate affects mainly CeO_x NSs of TL thickness or thinner.

The growth of a well-defined ceria film fully covering the Pt(111) substrate cannot be achieved simply by reactive deposition of evaporating Ce atoms in O₂ at elevated temperatures. Rather, a two-step kinetically limited growth procedure needs to be employed in order to obtain a full CeO₂(111) layer covering the Pt(111) substrate. Interestingly, a surface of CeO₂(100) could be achieved when ~3–4 MLE CeO_x was deposited onto Pt(111) and the surface was annealed in UHV at 1000 K. At the CeO_x film surface, the lower layer (the third layer) displays the c-Ce₂O₃(100) phase, which serves as a buffer layer for the growth of CeO₂(100) at the top layer (the fourth layer). The c-Ce₂O₃(100) buffer layer is formed via high-temperature reduction facilitated by the strong electronic interaction between CeO_x and Pt(111). A (3×*n*) reconstruction could be observed on the surface of the fourth layer of CeO_x. On top of the CeO_x film surface, there were also ceria nanoislands, which exhibit the (1×1)-CeO₂(100) surface lattice. After annealing at 900 K in 2×10⁻⁷ mbar O₂, the surface of the CeO₂(100) thin film is transformed into the hexagonal CeO₂(111) surface. Therefore, the structural dynamics and transition observed on CeO_x NSs and thin films on Pt(111) are determined by the competition between the interlayer interaction of CeO_x and the Pt-CeO_x interaction. Our study provides model systems for further catalytic

studies of ceria catalysts and enables molecular-level studies of facet-dependent catalysis of ceria and Pt/CeO_x catalysts.

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Graphical Abstract

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Interface-controlled synthesis of CeO₂(111) and CeO₂(100) and their structural transition on Pt(111)

Yi Zhang, Wei Feng, Fan Yang*, Xinhe Bao*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Science and Technology on Surface Physics and Chemistry Laboratory; University of Chinese Academy of Sciences

Ultrathin ceria films on Pt(111) usually exhibit the CeO₂(111) surface under oxidative conditions, but could form the CeO₂(100) surface upon UHV annealing at 1000 K owing to the strong interaction between ceria and Pt.

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CeO₂(111)和CeO₂(100)的界面调控合成及在Pt(111)上的结构转变

张毅^{a,c}, 冯卫^b, 杨帆^{a,*}, 包信和^{a,#}

^a中国科学院大连化学物理研究所催化基础国家重点实验室, 辽宁大连116023

^b表面物理与化学重点实验室, 四川江油621908

^c中国科学院大学, 北京100049

摘要: 氧化铈基催化材料在催化反应中存在显著的晶面效应, 为了在分子尺度上理解其催化化学, 需要可控合成具有明确表面结构的氧化铈。因此, 我们研究了Pt(111)上氧化铈纳米结构和薄膜的生长。人们通常使用金属-氧化物之间的强相互作用来解释Pt/CeO_x催化剂上的催化过程, 然而对于Pt与CeO_x之间的强相互作用仍旧缺乏原子尺度上的了解。我们的结果

表明, Pt与氧化铈之间的相互作用可以影响氧化铈的界面结构, 这可能会进而影响Pt/CeO_x催化剂的性质.

在Pt(111)上生长的氧化铈薄膜通常暴露CeO₂(111)表面. 我们发现Pt(111)表面厚度在三层以内的氧化铈薄膜, 其结构是高度动态且随着退火温度升高而变化的, 这种动态结构变化可归因于Pt和氧化铈间的界面电子作用. 当氧化铈薄膜的厚度增大到三层以上, 其负载的氧化铈团簇开始表现出迥异于三层以下氧化铈纳米岛的优异的热稳定性, 表明Pt与CeO_x之间的界面电子作用主要影响厚度在三层以内的氧化铈纳米结构. 采用常规的反应沉积方法难以获得完全覆盖Pt(111)衬底的规整氧化铈薄膜, 而我们通过采取一种两步的动力学限制生长方法, 制备出了完全覆盖Pt(111)衬底的氧化铈薄膜. 对于Pt(111)上厚度约为3–4层的氧化铈薄膜, 在超高真空中于1000 K退火会导致氧化铈薄膜表面形成CeO₂(100)结构. 这是因为高温还原促进了c-Ce₂O₃(100)缓冲层的形成, 该缓冲层被Pt的界面电子转移以及相匹配的超晶格所稳定, 并进一步成为顶层CeO₂(100)结构生长的模板. 进一步在900 K的氧气中处理则可将薄膜CeO₂(100)表面完全转变为CeO₂(111)表面.

因此, Pt(111)上氧化铈纳米岛和薄膜所展现的结构动态变化是由Pt-CeO_x界面作用与氧化铈层间作用相互竞争所决定. 本研究提供了对氧化铈负载Pt催化剂的原子级理解, 虽然Pt/CeO₂催化剂活性增强的原因常被简单归结于界面强相互作用, 我们的研究在原子尺度上进一步表明Pt/CeO₂在还原条件下易形成界面Ce₂O₃层. 此外, 本研究提供了不同晶面二氧化铈模型催化剂的构筑方法, 可将氧化铈晶面效应和Pt/CeO_x催化剂的研究推进到分子尺度.

关键词: 界面作用; Pt/CeO_x催化剂; CeO₂(111); CeO₂(100); c-Ce₂O₃(100)

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*通讯联系人. 电话: (0411)84379765; 传真: (0411)84694447; 电子信箱: fyang@dicp.ac.cn

#通讯联系人. 电话: (0411)84686637; 传真: (0411)84694447; 电子信箱: xhbao@dicp.ac.cn

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