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Two-dimensional, high valence-doped ceria: $Ce_6WO_{12}(100)/W(110)$

Vitalii Stetsovych, Tomáš Skála, Jan Beran, Filip Dvořák, Daniel Mazur[1], Nataliya Tsud, Karel Mašek, Josef Mysliveček*, Vladimír Matolín

Charles University in Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 180 00 Praha 8, Czech Republic

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ABSTRACT

Doping of oxides for catalytic applications represents one of the most used strategies for improving their catalytic performance. Model catalyst systems for doped oxides that would contain the dopant atoms in a well-defined geometry allowing for investigation of relationships between structure and reactivity are however rare. Here we report on preparation and structural properties of two-dimensional W-doped ceria on W(110) substrate. This model system adopts geometry of two-dimensional Ce_6WO_{12} (100)-oriented thin film, including isolated W^{6+} ions that donate the charge to Ce^{3+} ions and act as high-valence dopants. The system represents a model catalyst for prospective use in investigating the role of W^{6+} active sites in CeO_x-WO_x catalysts and high valence dopants in ceria in general.

1. Introduction

Cerium oxide – ceria – represents one of the most universal catalytic materials [1]. Its versatility in applications can be further enhanced by creating mixed and/or doped binary oxide systems where ceria coexists or forms solid solutions with another metal oxide [2–5]. In combination with tungsten oxide, ceria represents a prospective catalyst for production of hydrogen from methane [6], selective catalytic reduction of NO_x [7–9], or synthesis of organic molecules [10,11].

Physicochemical principles underlying high activity of particular catalysts are often studied on so called thin film model systems [12,13] that isolate well-defined structural, electronic and chemical aspects of real catalysts and allow to identify relationships between catalyst structure and reactivity. Proof-of-principle model catalysis studies on thin films of doped ceria are appearing [14–17] including cerium-tungsten systems or cerium tungstates [18,19]. Dopants in ceria can be classified based on their own stable oxidation state relative to Ce^{4+} oxidation state as low-, same-, or high-valence dopants [20].

Here we investigate growth mode, morphology and crystal structure of cerium tungstate Ce_6WO_{12} layers deposited on O-terminated W(110) single crystalline substrate [18]. Ce_6WO_{12} follows a Stranski-Krastanov growth mode when initially an ordered two-dimensional (2D) interfacial layer of Ce_6WO_{12} is formed. On top of the interfacial layer three-dimensional (3D) growth of amorphous Ce_6WO_{12} is observed. We find preparation conditions when the nucleation of 3D amorphous Ce_6WO_{12} is suppressed and the W(110) surface is completely covered by the 2D interfacial layer forming two-dimensional nanooxide Ce_6WO_{12}.

2. Experimental details

The experiment was performed on two surface science apparatuses, at the Materials Science Beamline at the Elettra synchrotron, Italy [X-ray photoelectron spectroscopy (PES), synchrotron radiation PES, resonant PES, low energy electron diffraction (LEED)], and in the Surface Physics Laboratory at the Charles University in Prague [scanning tunneling microscopy (STM), X-ray PES, LEED]. Both systems allow in-situ preparation and characterization of samples by a combination of surface sensitive experimental techniques. The substrate was a tungsten crystal (MaTecK) cut and polished with accuracy better than 0.1° and surface roughness below 30 nm. It was cleaned by Ar^+ sputtering and flash-annealing at 1373 K. Such surface is long-term unstable even in UHV environment, therefore it was annealed at 1073 K in 5×10^{-5} Pa of O_2 for 2 min in order to remove carbon contamination and to passivate the surface by a stable WO layer [21,22]. We note that such layer would anyway grow immediately at the beginning of the subsequent cerium deposition (under our conditions in less than 3 s).

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* Corresponding author.
E-mail address: josef.myslivecek@mff.cuni.cz (J. Mysliveček).

[1] Present address: CERIC-ERIC, S.S. 14 – km 163,5 in AREA Science Park, 34149 – Basovizza, Trieste, Italy.

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For determination of the growth mode of Ce_6WO_{12} on O-terminated W(110) and for identification of the suitable conditions for the 2D growth of Ce_6WO_{12} cerium oxide films were prepared by reactive deposition of Ce in the oxygen background pressure of 5×10^{-5} Pa and substrate temperature of 873 K or 1073 K. Eventually, the deposited layer was further treated by annealing in the oxygen background pressure of 5×10^{-5} Pa at temperatures up to 1200 K. The substrate temperature and the oxygen pressure were stabilized 1 min before the beginning of Ce deposition. Ce was evaporated from an electron bombardment-heated Ta crucible. The deposition amount was controlled by quartz crystal microbalance as well as by attenuation of the substrate W 4f core level intensities in XPS [23]. Deposition rate was set to 10 CeO_2 monolayers (ML) per hour. In the present work, 1 ML represents the density of Ce atoms in (111) plane of CeO_2, i.e. 7.9×10^{14} cm^{-2}.

The LEED images were acquired with electron energies 60 and 70 eV using a CCD camera. Lattice parameter of the deposit was calculated from the distances of diffraction spots which were determined by means of subpixel detection method with precision better than 0.5% [24]. For the photoemission Al Kα anode of the X-ray source (1487 eV; Ce 3d and O 1s core levels) and 220 eV monochromatized synchrotron beam (W 4f core level) were used. With respect to the off-line photon source the synchrotron radiation provided better total energy resolution (0.2 instead of 1 eV), higher cross sections (factor 43 [25]), higher surface sensitivity (factor 4 [26]) and an efficient damping of the partially overlapping W 4f and W $5p_{3/2}$ states (2% of the W 4f state instead of 8% [25]). Resonant valence band spectra were acquired with photon energies 115 eV (off-resonance), 121.4 eV (resonance of the Ce^{3+} states around the binding energy 1.5–2.5 eV) and 124.8 eV (resonance of the Ce^{4+} states around the binding energy 4–5 eV) [14].

3. Results and discussion

3.1. Growth mode of Ce_6WO_{12}

Growth of ordered thin films of Ce_6WO_{12} on O-terminated W(110) was identified and described by Skála et al. [18]. We observe the morphology and the electronic structure of the growing Ce_6WO_{12} thin film on O-terminated W(110) as a function of the film thickness by STM, LEED and PES of Ce 3d and W 4f emission lines. The results are shown in Fig. 1. PES of W 4f measured at $h\nu = 1487$ eV (Fig. 1f) was complemented with high-resolution measurement of W 4f at $h\nu = 220$ eV (Fig. 1g). Before the Ce deposition, O-terminated W(110) surface exhibits clean 10–20 nm wide terraces with a characteristic texture of bright stripes ∼2.6 nm apart (Fig. 1a) [27], a corresponding LEED pattern of a so-called 1 × 1 × 12 surface reconstruction related to the O-termination of W(110) [21], and W^0 and W^{2+} signals corresponding to O-terminated W(110) surface in PES (Fig. 1f, g). Further observations were performed upon deposition of 0.3 nm, 0.6 nm, and 1.2 nm thick Ce_6WO_{12} film (Fig. 1b–d). At submonolayer coverage (0.3 nm) the Ce_6WO_{12} film nucleates in the form of ordered 2D layer with distinct square pattern observed in STM and accompanied with the appearance of the square LEED pattern next to the 1 × 1 × 12 spots of the O-terminated substrate (Fig. 1b). For thicker films (0.6 nm and 1.2 nm) nucleation of the ordered Ce_6WO_{12} is completed and nucleation of a disordered layer progressively covering the ordered Ce_6WO_{12} phase is observed in both STM and LEED, (Figs. 1c, d). PES spectra of Ce 3d and W 4f shows only Ce^{3+} and W^{6+} contribution for the investigated film thicknesses (0.3–1.2 nm) suggesting Ce_6WO_{12} stoichiometry of both the ordered and the disordered Ce_6WO_{12} phases (Fig. 1e–g). The stoichiometry is confirmed by fitting the W^{6+} peak areas in W 4f spectra and comparing them, with consideration of the corresponding sensitivity factors, to the areas of Ce^{3+} peaks in Ce 3d spectra. This procedure yields Ce:W concentration ratio 5 ± 1 for Ce_6WO_{12} films between 0.3 and 1.2 nm thickness [18]. The growth mode of Ce_6WO_{12} on O-terminated W(110) thus follows a Stranski-Krastanov scenario when initially an ordered 2D interfacial layer of Ce_6WO_{12} is formed. On top of the interfacial layer 3D growth of amorphous Ce_6WO_{12} is observed. Nucleation of the amorphous 3D Ce_6WO_{12} clusters begins before the 2D interfacial layer completely covers the substrate (Fig. 1b).

With increasing Ce_6WO_{12} film thickness the intensity of the W^{6+} signal in the W 4f spectrum is increasing, while that of W^{2+} and W^0 signals is decreasing (Fig. 1f, g). This confirms that W atoms diffuse from the W substrate into the growing ceria layer and form a ternary cerium-tungsten mixed oxide covering the O-terminated W(110) surface as confirmed also by a recent PES study [28]. At film thickness of about 2 nm, W^{6+} amount in the Ce_6WO_{12} film stops increasing and further deposition of Ce results in nucleation of CeO_2 on top of the Ce_6WO_{12} thin film [18], accompanied by appearance of Ce^{4+} oxidation state in the Ce 3d spectra (Fig. 1e).

3.2. Two-dimensional Ce_6WO_{12}

We find that during high temperature treatment the amorphous 3D Ce_6WO_{12} is destabilized and only 2D interfacial layer of Ce_6WO_{12} remains on the O-terminated W(110) substrate. The 2D interfacial layer of Ce_6WO_{12} can fully cover the O-terminated W(110) surface. Morphology and LEED diffraction pattern of a sample exhibiting the full coverage with 2D interfacial layer of Ce_6WO_{12} obtained by annealing of the sample from Fig. 1d in 5×10^{-5} Pa of O_2 at 1300 K is shown in Fig. 2. During annealing, the thickness of the sample as determined with PES decreases from 1.2 nm to 0.5 nm indicating evaporation of the 3D Ce_6WO_{12} phase. Alternatively, 2D Ce_6WO_{12} samples exhibiting the full coverage of the O-terminated W(110) surface with 2D interfacial layer of Ce_6WO_{12} (i.e. LEED as in Fig. 2d with the absence of 1 × 1 × 12 spots of the O-terminated W(110) substrate, and thickness of 0.5 nm in PES) can be prepared directly by deposition of Ce on O-terminated W(110) in 5×10^{-5} Pa of O_2 and substrate temperature of 1073 K when the 3D nucleation of Ce_6WO_{12} is suppressed. Electronic structure of such sample equivalent to sample on Fig. 2 is shown in Fig. 3. This indicates that 2D Ce_6WO_{12} layer on O-terminated W(110) is an equilibrium structure independent of the preparation history and can be considered as an interface stabilized 2D nanooxide [29,30].

2D Ce_6WO_{12} layer on O-terminated W(110) exhibits two types of superstructures visible in STM (Fig. 2a). Superstructure I is represented by parallel dark lines running predominantly in vertical direction in Figs. 2a and b, and partially also in the horizontal direction in Fig. 2a. The spacing of the lines is irregular and varying between 4 and 9 nm. Superstructure I is marked by full blue lines in Figs. 2a and b. Superstructure II is represented by fainter streaks running diagonally in Figs. 2a and b. Superstructure II is marked by dotted blue lines in Figs. 2a and b. On the high resolution STM image in Fig. 2c, square periodic pattern of the 2D Ce_6WO_{12} layer is observed. On the LEED image of the 2D Ce_6WO_{12} layer (Fig. 2d) we can identify diffraction spots of the reciprocal surface unit cell (red outline), determining the lattice constant of ∼1.25 nm and marked in real space in Fig. 2c. LEED patterns corresponding to superstructures I and II are also marked in Fig. 2d. Diagonally running superstructure II causes diffraction spots on the diagonal of the reciprocal 2D Ce_6WO_{12} unit cell (marked by dotted blue line in Fig. 2d). Finally, the irregularly spaced superstructure I causes streaks in the vertical and horizontal directions decorating the LEED diffraction spots in Fig. 2d (marked by full blue lines).

The electronic structure of the 2D Ce_6WO_{12} layer on O-terminated W(110) is shown in Fig. 3. The Ce 3d spectrum (Fig. 3a) after the numerical subtraction of the X-ray satellites exhibits only Ce^{3+} components. The O 1s spectrum (Fig. 3b) shows a single peak