[Article]

doi: 10.3866/PKU.WHXB201804092

www.whxb.pku.edu.cn

Morphologies and Electronic Structures of Calcium-Doped Ceria Model Catalysts and Their Interaction with CO₂

WANG Yan, LI Xiong, HU Shanwei^{*}, XU Qian, JU Huanxin, ZHU Junfa^{*}

National Synchrotron Radiation Laboratory, Department of Chemical Physics, University of Science and Technology of China, Hefei 230029, P. R. China.

Abstract: CeO₂-based catalysts are promising for use in various important chemical reactions involving CO₂, such as the dry reforming of methane to produce synthesis gas and methanol. CeO₂ has a superior ability to store and release oxygen, which can improve the catalytic performance by suppressing the formation of coke. Although the adsorption and activation behavior of CO₂ on the CeO₂ surface has been extensively investigated in recent years, the intermediate species formed from CO₂ on ceria has not been clearly identified. The reactivity of the ceria surface to CO₂ has been reported to be tuned by introducing CaO, which increases the number of basic sites for the ceria-based catalysts. However, the mechanism by which Ca²⁺ ions affect CO₂ decomposition is still debated. In this study, the morphologies and electronic properties of stoichiometric CeO₂(111), partially reduced CeO_{2-x}(111) (0 < x < 0.5), and calcium-doped ceria model catalysts, as well as their interactions with CO₂, were investigated by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy, and synchrotron radiation photoemission spectroscopy. Stoichiometric CeO₂(111) and partially reduced CeO_{2-x}(111) films were epitaxially grown on a Cu(111) surface. STM images show that the stoichiometric CeO₂ film exhibits large, flat terraces that completely cover the Cu(111) surface. The reduced CeO_{2-x} film also has a flat surface and an ordered structure, but dark spaces are observed on the film. Different Ca-doped ceria films were prepared by physical vapor deposition of metallic Ca on CeO₂(111) at room temperature and subsequent annealing to 600 or 800 K in ultrahigh vacuum. The different preparation procedures produce samples with various surface components, oxidation states, and structures. Our results indicate that the deposition of metallic Ca on CeO₂ at room temperature leads to a partial reduction of Ce from the +4 to the +3 state, accompanied by the oxidation of Ca to Ca²⁺. Large CaO nanofilms are observed on CeO₂ upon annealing to 600 K. However, small CaO nanoislands appear near the step edges and more Ca²⁺ ions migrate into the subsurface of CeO₂ upon annealing to 800 K. In addition, different surface-adsorbed species are identified after CO₂ adsorption on ceria (CeO₂ and reduced CeO_{2-x}) and Ca-doped ceria films. CO₂ adsorption on the stoichiometric CeO₂ and partially reduced CeO_{2-x} surfaces leads to the formation of surface carboxylate. Moreover, the surface carboxylate species is more easily formed on reduced CeO_{2-x} with enhanced thermal stability than on stoichiometric CeO₂. On Ca-doped ceria films, the presence of Ca²⁺ ions is observed to be beneficial for CO₂ adsorption; further, the carbonate species is identified.

Key Words: Calcium; Ceria; Scanning tunneling microscopy; X-ray photoelectron spectroscopy; Synchrotron radiation photoemission spectroscopy

Received: March 14, 2018; Revised: April 2, 2018; Accepted: April 3, 2018; Published online: April 9, 2018.

^{*}Corresponding authors. Email: husw@ustc.edu.cn (H.S.); jfzhu@ustc.edu.cn (Z.J.); Tel.: +86-551-63602064.

The project was supported by the National Natural Science Foundation of China (U1732272, 21473178, 21403205), National Key Technologies R&D Program of China (2017YFA0403402), and China Postdoctoral Science Foundation (BH2310000032).

国家自然科学基金(U1732272, 21473178, 21403205), 国家重点研发计划(2017YFA0403402)和中国博士后科学基金(BH2310000032)资助项目

© Editorial office of Acta Physico-Chimica Sinica

Ca 掺杂的 CeO₂ 模型催化剂的形貌和电子结构及其与 CO₂ 分子的相互作用

王岩, 李雄, 胡善玮*, 徐倩, 鞠焕鑫, 朱俊发*

中国科学技术大学化学物理系, 国家同步辐射实验室, 合肥 230029

摘要: 利用扫描隧道显微镜、X射线光电子能谱和同步辐射光电子能谱研究了CeO₂(111), 部分还原的CeO_{2-x}(111) (0 < x < 0.5)以及Ca掺杂的CeO₂模型催化剂的形貌、电子结构以及它们与CO₂分子间的相互作用。CeO₂(111)和部分还原的CeO_{2-x}(111)薄膜外延生长于Cu(111)单晶表面。不同Ca掺杂的CeO₂薄膜是通过在CeO₂(111)薄膜表面室温物理沉积金属Ca及随后真空退火到不同温度而得到的。不同的制备过程导致样品具有不同的表面组成, 化学态和结构。CO₂吸附到CeO₂和部分还原的CeO_{2-x}表面后导致表面羧酸盐的形成。此外, 相比于CeO₂表面, 羧酸盐物种更易在部分还原的CeO_{2-x}表面生成, 而且更加稳定。而在Ca掺杂的氧化铈薄膜表面, Ca²⁺离子的存在有利于CO₂的吸附, 且探测到碳酸盐物种的形成。

关键词: 钙; 二氧化铈; 扫描隧道显微镜; X射线光电子能谱; 同步辐射光电子能谱

中图分类号: O643

1 Introduction

Carbon dioxide is of particular interests since it can be utilized in numerous chemical processes, such as dry reforming of methane (CH₄ + CO₂) to produce synthesis gas (CO + H₂) and methanol synthesis^{1,2}. However, the metal catalysts involving in these reactions undergo serious deactivation due to the coke formation³. The use of ceria-based catalysts can alter this situation. CeO₂ has superior oxygen storage/release capacity, resulting in the self-cleaning properties of the catalysts that carbon is oxidized by the oxygen from the CeO₂ surface⁴. It is therefore understandable that the interaction between the CeO₂ surface and CO₂ has extensively been investigated in the literatures⁵⁻⁸. However, the intermediate species formed from CO₂ on ceria is yet unclear. Moreover, it is reported that the reactivity of ceria surface to CO₂ can be tuned by introducing CaO, which increases the basic sites for ceria-based catalysts⁹. It has been investigated that CO₂ could chemisorb at a regular surface site of CaO, leading to the formation of carbonates¹⁰⁻¹². Although the presence of Ca improves the catalytic performance of ceria-based materials in reactions involving CO₂, however, the mechanism of the effect of Ca²⁺ ions on CO₂ decomposition is still under debate. For example, Kang *et al.*¹³ reported that the adding of Ca²⁺ into ceria-based solid solutions could enhance the oxygen mobility which might account for the improved CO₂ splitting reactivity. However, the synergistic effect between Ca²⁺ and Ce³⁺ ions was identified on CaO-CeO₂ based oxides to enhance the CO₂ activation¹⁴. Moreover, the fundamental-level investigation of the interaction of CO₂ with CaO-CeO₂ surfaces is still lacking, which motivates our current study.

In this work, we investigated the morphologies and electronic structures of stoichiometric CeO₂(111), reduced CeO_{2-x}(111) (0 < x < 0.5), and Ca-doped CeO₂ model catalysts and their interaction with CO₂ by scanning tunneling microscopy (STM),

X-ray photoelectron spectroscopy (XPS), and synchrotron radiation photoemission spectroscopy (SRPES). It is observed that CO₂ adsorption on ceria (CeO₂ and reduced CeO_{2-x}) and Ca-doped CeO₂ surfaces exhibits different adsorbed species. Ca-doped CeO₂ films show different surface structures at different annealing temperatures, which results in different adsorption behaviors of CO₂. Moreover, the presence of Ca in Ca-doped CeO₂ films enhances the CO₂ adsorption.

2 Experimental

The experiments were carried out in two separate ultrahigh vacuum (UHV) systems. STM measurements were performed in a system that comprises three chambers with base pressures all below 1 × 10⁻⁸ Pa. The XPS and SRPES measurements were carried out on the Catalysis and Surface Science Endstation at BL11U beamline in the National Synchrotron Radiation Laboratory, Hefei. These two systems have been described in detail previously^{15,16}. Briefly, the beamline is connected to an undulator and equipped with two gratings that cover photon energies from 20 to 600 eV with a resolution ($E/\Delta E$) better than 10⁴ at 29 eV. All the STM images were recorded at room temperature with the bias of 3–4 V and tunneling current of 0.01–0.05 nA using an etched tungsten tip. The WSXM program¹⁷ was used to process the STM images. Core level spectra of Ce 3d, Ca 2p, and O 1s were acquired with a monochromatic X-ray source using Al K_α radiation (1486.6 eV) (SAX 100, VG Scienta, Sweden). Moreover, Ca 2p and C 1s spectra were obtained with a photon energy of 420 eV, while valence band (VB) spectra were measured at $h\nu = 115$ eV. All spectra were measured at 0° with respect to the surface normal.

The CO₂ (99.999%, Wuhan Newradar Special Gas CO., LTD.) adsorption was performed in 10 L doses (6.5 × 10⁻⁶ Pa, 260 s) at 180 K by backfilling the UHV chamber.

The Cu(111) single crystal (8 mm diameter and 2 mm thickness), purchased from Mateck GmbH, Germany, was used as the substrate. Cu(111) was cleaned by repeated cycles of Ar⁺ sputtering and annealing until no contaminant could be found by XPS, and a sharp (1 × 1) LEED pattern was achieved. In this work, we prepared two ceria films, which were CeO₂(111)/Cu(111) and reduced CeO_{2-x}(111) (0 < x < 0.5), and three Ca-doped ceria films, including Ca/CeO₂, Ca/CeO₂-600 K and Ca/CeO₂-800 K. The preparation procedures were as follows.

CeO₂(111)/Cu(111). Stoichiometric CeO₂(111) films were grown on a clean Cu(111) substrate at gradually increased substrate temperature by physical vapor deposition of Ce metal (99.9%, Alfa Aesar, USA) from an electron beam evaporator (EBE-4, Specs, Germany) in 4 × 10⁻⁵ Pa oxygen (99.999%, Nanjing Shangyuan). After deposition, the films were post-annealed at 850 K for 10 min in the same oxygen pressure. The monolayer (ML) of the ceria film is defined as O-Ce-O stack normal to the (111) plane with a thickness of 0.31 nm¹⁸.

CeO_{2-x}(111) (0 < x < 0.5). The partially reduced CeO_{2-x}(111) films were obtained at a lower oxygen pressure of 9 × 10⁻⁶ Pa during the Ce deposition followed by annealing in UHV. The ceria films were 2–4 nm thick.

Ca/CeO₂. The sample of Ca/CeO₂ was prepared by deposition of 1.2 ML Ca on CeO₂(111) at room temperature. Ca (99.5%, Alfa Aesar, America) was physical vapor deposited on the CeO₂ surface from a homemade evaporator with the evaporation rate of 0.2 ML·min⁻¹. The Ca flux was calibrated with a quartz crystal microbalance (QCM) (TMC 13, Prevac, Poland) before deposition. One ML of Ca is defined as 7.9 × 10¹⁴ atoms·cm⁻²,

which is the number of oxygen atoms per unit area in the topmost atomic layer of the CeO₂(111) surface¹⁹.

Ca/CeO₂-600 K and Ca/CeO₂-800 K. The samples, Ca/CeO₂-600 K and Ca/CeO₂-800 K, were obtained by heating Ca/CeO₂ to 600 and 800 K in UHV, respectively.

3 Results and discussion

3.1 Characterization of Ceria-Based Model Catalysts

Firstly, we studied the surface morphologies and electronic structures of ceria-based catalysts. STM images of all samples are displayed in Fig. 1. As shown in Fig. 1a, the stoichiometric CeO₂ film exhibits large and flat terraces that completely cover the Cu(111) surface. The apparent height of CeO₂ islands is measured to be 0.30 nm, in agreement with the spacing of O-Ce-O trilayers in the fluorite bulk CeO₂(111) structure (0.31 nm)¹⁸. As displayed in the atomic-scale resolution STM image (inset of Fig. 1a), CeO₂ displays a well-ordered atomic structure. The measured distance between two adjacent Ce atoms is 0.39 nm, which is consistent with 0.383 nm, the expected surface spacing for Ce-Ce in the bulk CeO₂(111)²⁰. Reduced CeO_{2-x} film also has a flat surface and an ordered structure, however, dark spaces are observed on the surface (Fig. 1b). The nature of dark spaces is attributed to the surface defects, which are associated with the missing lattice oxygen atoms or holes^{18,20–22}. After the CeO₂ surface was deposited 1.2 ML Ca at room temperature, the CeO₂ surface is fully covered by Ca islands, as seen in Fig. 1c. The line scan profile shown in the inset of Fig. 1c suggests that the heights of deposited Ca islands are less than 2.5 Å (1 Å = 0.1 nm). Fig. 1d shows the morphological information of Ca/CeO₂-600 K.

Fig. 1 STM images (130 nm × 130 nm) of samples: (a) CeO₂(111), (b) CeO_{2-x}(111), (c) Ca/CeO₂, (d) Ca/CeO₂-600 K, and (e) Ca/CeO₂-800 K. The insets of (a) and (b) show the high-resolution STM images (4.8 nm × 4.8 nm) of CeO₂(111) and CeO_{2-x}(111), respectively. Panels (c)–(e) include the line scans along the corresponding Ca islands on ceria. (f) Magnified STM image (6.5 nm × 6.5 nm) of the black framed region in panel (e), showing the detailed structure of the CeO₂ substrate for Ca/CeO₂-800 K.

Heating the room temperature deposited Ca on CeO₂ to 600 K leads to the aggregation of small Ca islands to large area Ca islands and part of CeO₂ substrate is exposed. As seen in the inset of Fig. 1d, a line scan profile across a large Ca island indicates that the Ca island is more than 10.0 Å high. On Ca/CeO₂-800 K (Fig. 1e), more exposed CeO₂ is observed and small Ca islands are accumulated near terrace step edges. The line scan profile shows that the heights of Ca islands decrease to less than 2.0 Å (inset of Fig. 1e). Compared with that on Ca/CeO₂-600 K, the amount of Ca nanoparticles on the surface of Ca/CeO₂-800 K decreases. Furthermore, oxygen vacancies are observed on Ca/CeO₂-800 K (Fig. 1f).

To identify the electronic structures of the ceria-based model catalysts, high resolution core-level spectroscopies were investigated. Fig. 2a–c display the Ce 3d and Ca 2p core-level spectra of the studied samples. As shown in Fig. 2a, six peaks are identified in the Ce 3d spectrum of the CeO₂(111) film, which correspond to three pairs of spin-orbit split doublets arising from photoemission from Ce⁴⁺ ions^{23,24}. In the Ce 3d spectrum of reduced CeO_{2-x}, four more peaks emerge and are labeled as u₀, u', v₀, and v', which are typical peaks for Ce³⁺ ions²³. By fitting the Ce 3d spectrum based on the procedure introduced by Skala^{25,26}, the percentage of Ce³⁺ in CeO_{2-x} can be determined, which is 0.259 (Fig. 2d). Thus this CeO_{2-x} film is assigned to CeO_{1.87}. The increase of Ce reduction in ceria suggested by XPS agrees well with the increase in the number of oxygen vacancies observed by STM.

On Ca/CeO₂, the typical peaks for Ce³⁺ are also visible in the Ce 3d spectrum. After fitting this Ce 3d spectrum, the fraction of Ce³⁺ in Ca/CeO₂ is calculated to be 0.279 (Fig. 2d). This indicates that partial reduction of ceria occurs upon Ca deposition, which matches with the Ca 2p XPS study shown in Fig. 2b, c. As seen in Fig. 2b, the Ca 2p spectrum of Ca/CeO₂ can be easily fitted with one pair of spin-orbit split doublet that is 3.5 eV apart. The Ca 2p_{3/2} at 346.9 eV is compatible with the reported values for CaO^{27–29}, suggesting that Ca is oxidized to

Ca²⁺ on CeO₂. This process can be depicted as $\text{Ca} + 2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{CaO}$, which is expected from thermodynamics. Based on ΔH_f^{298} of oxide formation energy³⁰, this process is favored by 253 kJ·mol⁻¹ at room temperature. Therefore, the Ca islands on CeO₂ observed by STM image (Fig. 1c) are attributed to CaO nanoislands. However, CaO film is assembled by the repeating O-Ca-O trilayer^{31,32}, and a complete O-Ca-O trilayer is 4.8 Å in height³¹, which is larger than the thickness of Ca islands (less than 2.5 Å). Therefore, the CaO nanoislands are proposed to be Ca terminated, forming a Ce-O-Ca mixed layer at the Ca-CeO₂ interface. This phenomenon is similar to the case of Zr^{16,33}, Al³⁴, Sn^{25,35}, and Mn³⁶ on CeO₂(111).

Compared with those from Ca/CeO₂, the characteristic peaks related to Ce³⁺ in the Ce 3d region of Ca/CeO₂-600 K are attenuated, while those due to Ce⁴⁺ are intensified (Fig. 2a). Although the Ca 2p peak of Ca/CeO₂-600 K shifts to a lower binding energy (Fig. 2b), it still can be assigned to Ca²⁺ ions, which bond to O²⁻. This shift may be attributed to the size and structure changes, as seen in STM images (Fig. 1c, d), after annealing. As mentioned above, the thickness of large Ca islands is two times higher than that of an O-Ca-O trilayer (Fig. 1d), suggesting the formation of CaO nanofilms with at least two layers thick. The oxygen in these CaO nanofilms should come from the lattice oxygen of CeO₂. However, compared to Ca/CeO₂, the Ce³⁺ fraction in Ca/CeO₂-600 K even decreases about ~14% (from 0.28 to 0.244) (Fig. 2d). Similar phenomena were observed on Pt-ceria³⁷ and W-ceria³⁸ interface upon heating, where the decrease of Ce³⁺ concentration was attributed to the Ce³⁺ migration into deeper layers³⁷ or the compensation of surface oxygen vacancies by bulk oxygen³⁸. The fact that the heights of CaO nanofilms on Ca/CeO₂-600 K are higher than those of CaO nanoislands on Ca/CeO₂ suggests that oxygen atoms diffuse from the bulk to the surface.

On the Ca/CeO₂-800 K sample, the Ce 3d intensity increases compared with that of Ca/CeO₂-600 K. Moreover, Ce³⁺ concentration in Ca/CeO₂-800 K increases to 0.263 (Fig. 2d),

Fig. 2 Core level spectra of (a) Ce 3d and (b, c) Ca 2p from samples: CeO₂, CeO_{2-x}, Ca/CeO₂, Ca/CeO₂-600 K, and Ca/CeO₂-800 K.

(a) and (b) are collected with a photon energy of 1486.6 eV. (c) is acquired with a photon energy of 420 eV. (d) The values of $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ in samples: CeO₂(111), Ca/CeO₂, Ca/CeO₂-600 K, and Ca/CeO₂-800 K. (e) The integrated Ca 2p intensities of samples: Ca/CeO₂, Ca/CeO₂-600 K, and Ca/CeO₂-800 K collected at photon energies of 1486.6 and 420 eV.

suggesting that the CeO_2 substrate is more reduced. These results match well with the increase in the area of exposed ceria and surface defects indicated by STM images (Fig. 1e, f). On Ca/CeO_2 -800 K, the $\text{Ca } 2p$ peak is again assigned to Ca^{2+} . The $\text{Ca } 2p$ intensity decreases compared with that of Ca/CeO_2 and Ca/CeO_2 -600 K (Fig. 2b, c), which is related to the decrease in the Ca amount on the CeO_2 surface observed by STM (Fig. 1e). In addition, the decrease extent is varied between the $\text{Ca } 2p$ intensity collected at 1486.6 eV and that collected at 420 eV.

Fig. 2e displays the $\text{Ca } 2p$ intensities of Ca-doped samples collected at photon energies of 1486.6 and 420 eV. All the $\text{Ca } 2p$ intensities were normalized to the corresponding $\text{Ca } 2p$ intensities of Ca/CeO_2 . As can be seen, the $\text{Ca } 2p$ intensities collected at 1486.6 eV decrease to 0.993 on Ca/CeO_2 -600 K and 0.710 on Ca/CeO_2 -800 K, respectively. While the $\text{Ca } 2p$ intensities collected at 420 eV decrease to 0.965 on Ca/CeO_2 -600 K and 0.543 on Ca/CeO_2 -800 K, respectively. It is obvious that the $\text{Ca } 2p$ intensities collected at 420 eV decrease faster compared with those collected at 1486.6 eV. Given the fact that $\text{Ca } 2p$ spectra collected at 420 eV are more surface sensitive than those collected at 1486.6 eV, this result is ascribed to the oxygen migration from ceria to the top of Ca and the diffusion of Ca into ceria for Ca/CeO_2 -600 K and Ca/CeO_2 -800 K. Particularly, after annealing the Ca/CeO_2 sample to 800 K, more Ca diffuses into the subsurface of CeO_2 to form mixed CeO_2 - CaO oxide, which matches with the STM images (Fig. 1) and the observed intensity increase of $\text{Ce } 3d$.

3.2 Interaction of CO_2

Next we investigate the interaction of CO_2 with stoichiometric $\text{CeO}_2(111)$, reduced $\text{CeO}_{2-x}(111)$, Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K. These samples were exposed to 10 L CO_2 at 180 K and stepwise heated to higher temperatures in UHV. Fig. 3 illustrates the development of the $\text{C } 1s$ spectra from CeO_2 , CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K exposed with 10 L CO_2 at 180 K and subsequent heating to different temperatures. As shown in Fig. 3a and 3b, only one peak at 289.5 eV emerges in the $\text{C } 1s$ spectra after CO_2 exposed on CeO_2 and CeO_{2-x} at 180 K. However, compared with CeO_2 , the intensity of $\text{C } 1s$ is stronger on CeO_{2-x} , suggesting much more CO_2 can be adsorbed on the reduced ceria, in agreement with our previous study using IRAS⁵. Although the formation of surface carbonate (CO_3^{2-})^{6,39} and carboxylate (CO_2^-)⁴⁰ after CO_2 adsorption on ceria has been both reported in the literature, using IRAS we have confirmed the formation of carboxylate located over oxygen vacancies⁵. Therefore, we attribute the $\text{C } 1s$ peak at 289.5 eV to the surface carboxylate. Even on the stoichiometric $\text{CeO}_2(111)$, very small amount of oxygen vacancies exists, as demonstrated by angle-dependent XPS²¹. Therefore, it is understandable that on the reduced ceria surface, the amount of adsorbed CO_2 increases. Upon annealing, the $\text{C } 1s$ signal totally disappears at 260 K on $\text{CeO}_2(111)$, indicating the complete desorption of CO_2 from the surface. However, on partially reduced $\text{CeO}_{2-x}(111)$, the $\text{C } 1s$ peak disappears until the temperature increases to 500 K. This

Fig. 3 C 1s spectra obtained from samples: (a) CeO_2 , (b) CeO_{2-x} , (c) Ca/CeO_2 -600 K, and (d) Ca/CeO_2 -800 K upon 10 L CO_2 adsorption at 180 K and subsequent heating to higher temperatures.

suggests that carboxylates are more stable on reduced CeO_{2-x} than on the stoichiometric CeO_2 surface.

Similar to the observations on ceria surfaces, after 10 L CO_2 adsorption on Ca-doped ceria (i.e., Ca/CeO_2 -600 K and Ca/CeO_2 -800 K) at 180 K, also only one peak is observed in the $\text{C } 1s$ region. As shown in Fig. 3c and 3d, the $\text{C } 1s$ peak locates at 290.4 and 290.2 eV on Ca/CeO_2 -600 K and Ca/CeO_2 -800 K, respectively. According to the literature, carbonate species were observed upon CO_2 adsorption on CaO ^{11,12,41} and magnesia-ceria model catalysts^{39,42}. Moreover, carbonate was identified at 290 eV in $\text{C } 1s$ spectra on Mg-doped ceria⁴². Based on the above discussion, this peak is attributed to the carbonate species. However, it should be mentioned that the nature of the surface species needs more straightforward experimental evidences such as IRAS or theoretical calculations. Nevertheless, since the binding energies of $\text{C } 1s$ spectra from calcium carbonates are reported to be 289.7–291.9 eV^{43–46}, we ascribe the peaks at 290.4 and 290.2 eV to CO_3^{2-} formed near Ca^{2+} ions. After heating Ca/CeO_2 -600 K to 500 K, the $\text{C } 1s$ intensity slightly decreases, with no significant shift in binding energy. Further increasing the temperature to 700 K leads to a sharp decrease in the $\text{C } 1s$ intensity and a shift of the peak position towards a lower binding energy of 290.2 eV. On Ca/CeO_2 -800 K, between 260 and 500 K, the intensity of the peak associated with CO_3^{2-} species decreases monotonically and the binding energy shifts from 290.2 eV (180 K) to 290.3 eV (500 K). Up to 700 K, the peak vanishes in the $\text{C } 1s$ region.

Fig. 4a–c show the $\text{O } 1s$ spectra of CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K with CO_2 adsorption at 180 K and

Fig. 4 O 1s spectra obtained from samples: (a) CeO_{2-x} , (b) Ca/CeO_2 -600 K, and (c) Ca/CeO_2 -800 K upon 10 L CO_2 adsorption at 180 K and subsequent heating to higher temperatures. The O 1s spectra of CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K are plotted as top curves in (a)–(c), respectively. (d) Integrated C 1s intensities of CeO_2 , CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K (black) and the intensity ratios of O 1s peak γ to peak α of CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K (red) with 10 L CO_2 adsorption at 180 K as a function of temperature.

subsequent annealing to different temperatures, respectively. The O 1s spectra from CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K are shown at the top of each figure. As shown in Fig. 4a, the main peak obtained from CeO_{2-x} at 530.0 eV (peak α) appears due to lattice oxygen²³. A second component (peak β) emerges at 531.4 eV, which is attributed to O^{2-} near Ce^{3+} ²³. Exposing CO_2 to CeO_{2-x} at 180 K triggers the attenuation of peak α and the emergence of a new peak at 531.8 eV (peak γ). As the binding energy of peak γ is consistent with the reported values of carboxylate⁵, we assign peak γ to the CO_2^- species. Upon heating, the intensity of peak γ diminishes monotonically and the peak α increases. After the temperature increases to 500 K, the O 1s spectrum is similar to that of pure CeO_{2-x} , suggesting the CO_2 desorption from CeO_{2-x} .

As shown in Fig. 4b, one feature at 530.0 eV (peak α) appears on Ca/CeO_2 -600 K. This feature is associated with lattice oxygen of ceria. However, according to the literature⁴⁷, the O 1s peak of CaO was reported to be at 530.2 eV, which is close to peak of lattice oxygen of ceria. Thus, we cannot exclude the contribution of O^{2-} in CaO to peak α . Upon CO_2 adsorption at 180 K, a peak located at 533.0 eV (peak γ) emerges, which is related to CO_3^{2-} near Ca^{2+} ⁴⁶. Accordingly, the peak α decreases. Upon annealing, the intensity of carbonate O peak (peak γ) slightly decreases between 180 K and 500 K and then sharply decreases up to 700

K. Similarly, after CO_2 adsorption on Ca/CeO_2 -800 K at 180 K (Fig. 4c), a new feature associated with CO_3^{2-} near Ca^{2+} (peak γ) emerges at 532.2 eV. The different binding energies of carbonate O peaks for Ca/CeO_2 -600 K and Ca/CeO_2 -800 K are related to the adsorption of CO_2 on CaO and CeO_2 - CaO mixed oxide. Similar results have been reported for CO_2 adsorption on MgO/CeO_2 model catalysts⁴². Increasing annealing temperature leads to the decrease in the intensity of carbonate O peak. At 500 K, the intensity of the main peak at 530.0 eV (peak α) recovers to that of clean Ca/CeO_2 -800 K. The variations of peak α intensities of the studied samples upon CO_2 adsorption and subsequent annealing are due to the formation and decomposition of carboxylates on different ceria or carbonates on Ca-doped ceria.

In Fig. 4d, the C 1s and O 1s intensities for CeO_2 , CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K exposed with 10 L CO_2 are plotted as a function of temperature. It is seen that the intensities of C 1s after CO_2 adsorption formed on the four samples follows the order of Ca/CeO_2 -600 K > Ca/CeO_2 -800 K > CeO_{2-x} > CeO_2 , suggesting that the doping of calcium in CeO_2 enhances the CO_2 adsorption. Upon heating, all C 1s intensities start to decrease, indicating that the surface carboxylates or carbonates start to decompose. Moreover, on ceria surfaces, the C 1s intensities decrease much faster upon annealing than those on Ca-doped ceria surfaces, indicating that the surface carboxylates are less stable than carbonates.

The Ca 2p spectra of Ca/CeO_2 -600 K and Ca/CeO_2 -800 K upon CO_2 adsorption at 180 K and subsequent annealing are also investigated. As shown in Fig. 5, after CO_2 exposed on Ca/CeO_2 -600 K and Ca/CeO_2 -800 K, the Ca 2p spectra are broad and consist of two pairs of spin-orbit split doublets that are 3.5 eV apart. The main Ca 2p_{3/2} peak on both samples at 346.5 eV is assigned to Ca^{2+} in Ca-doped ceria. The shoulders at higher binding energies of 347.9 eV on Ca/CeO_2 -600 K and 347.3 eV on Ca/CeO_2 -800 K are ascribed to Ca^{2+} in CaCO_3 ^{29,48–50}. This indicates that Ca^{2+} ions on the Ca/CeO_2 -600 K and Ca/CeO_2 -800 K surfaces react with CO_2 to form CaCO_3 . Considering that more Ca^{2+} diffuses into ceria in the sample of Ca/CeO_2 -800 K, the

Fig. 5 Ca 2p spectra of (a) Ca/CeO_2 -600 K and (b) Ca/CeO_2 -800 K upon 10 L CO_2 adsorption at 180 K and subsequent heating to higher temperatures.

Fig. 6 VB spectra obtained from samples: (a) CeO_2 , (b) CeO_{2-x} , (c) Ca/CeO_2 -600 K, and (d) Ca/CeO_2 -800 K upon 10 L CO_2 adsorption at 180 K and subsequent heating to higher temperatures. The VB of CeO_2 , CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K are plotted as top curves in (a)–(d), respectively.

CaCO_3 -related Ca 2p peak is much weaker compared with that observed on Ca/CeO_2 -600 K. Upon annealing, the Ca 2p peaks related to CaCO_3 on both samples undergo slow decrease up to 500 K, followed by fast decrease. After 700 K annealing, almost no CaCO_3 -related Ca 2p peaks can be observed, suggesting that the CaCO_3 species completely decomposes. These results agree well with the C 1s and O 1s studies (Figs. 3, 4).

Fig. 6a–d display the VB spectra from CeO_2 , CeO_{2-x} , Ca/CeO_2 -600 K, and Ca/CeO_2 -800 K exposed with 10 L CO_2 at 180 K and subsequent annealing to different temperatures. The spectra of the studied samples are plotted as top curves in each figure. Note that the presented spectra were obtained with a photon energy of 115 eV, corresponding to the off-resonance condition⁵¹. The principle features of the VB spectrum measured in off-resonance mode from ceria have been discussed by Mullins *et al.*²³. The authors attributed two broad features at 4.5 and 6.5 eV to the O 2p orbitals hybridized with Ce 4f and 5d orbitals, respectively. Moreover, a feature is observed at 2–3 eV in the VBs of the studied samples. Matolin *et al.* reported that the features between 0.1 and 4.5 eV in the VB of continuous $\text{CeO}_2(111)/\text{Cu}(111)$ films were assigned to Ce 5d, 6s, 4f states of CeO_2 ^{52,53}. For CaO, no feature at 2–3 eV is reported to appear in the VB spectrum⁵⁴. Thus, the feature at 2–3 eV is related to the ceria films grown on Cu(111), which was also observed in some literatures when studying the VBs of ceria films grown on Cu(111)^{25,34,35,39,52,53}. Additional features appear in the VBs of CeO_2 and CeO_{2-x} upon CO_2 exposure at 180 K. On CeO_2 , a

feature appears at 9.7 eV (Fig. 6a); on CeO_{2-x} , two features appear at 10.1 eV and 12.2 eV, respectively (Fig. 6b). According to the literatures^{55,56}, they are related to the carboxylate species. After heating CeO_2 to 260 K, CO_2 desorbs from the surface, leading to the disappearance of the feature at 9.7 eV, in agreement with the observation of C 1s spectra shown in Fig. 3a. While the two features on CeO_{2-x} gradually decrease upon annealing and completely disappear up to 500 K, indicating that CO_2^- is much more stable on reduced CeO_{2-x} .

On Ca/CeO_2 -600 K (Fig. 6c) and Ca/CeO_2 -800 K (Fig. 6d), the broad feature at 5.0 eV in the VBs is attributed to O 2p from oxygen species involved in Ca–O bonds⁴⁶. The adsorption of CO_2 on both surfaces result in the appearance of three additional features: 6.5, 11.2 and 13.4 eV on Ca/CeO_2 -600 K and 6.2, 10.6 and 12.8 eV on Ca/CeO_2 -800 K; they are ascribed to the ($1a_2'$; $1e'$; $4e'$), ($3e'$; $1a_2'$), and $4a_1'$ molecular orbitals of CO_3^{2-} , respectively^{54,57}. Moreover, the evolution of these peaks with annealing temperatures agree well with those observations in the C 1s, O 1s and Ca 2p studies (Fig. 3–5). These results further support the formation of carboxylates on CeO_2 and reduced CeO_{2-x} and carbonates on Ca-doped ceria upon CO_2 adsorption. Moreover, the carboxylates formed on ceria are less stable than carbonates formed on Ca-doped CeO_2 samples. In addition, the carbonates on Ca/CeO_2 -800 K exhibit a lower thermal stability compared with those on Ca/CeO_2 -600 K.

4 Conclusions

We investigate the morphologies and electronic structures of stoichiometric $\text{CeO}_2(111)$, partially reduced $\text{CeO}_{2-x}(111)$ ($0 < x < 0.5$), and Ca-doped ceria model catalysts and their interaction with CO_2 using STM, XPS, and SRPES. Deposition of 1.2 ML Ca on $\text{CeO}_2(111)$ leads to the immediate reduction of Ce^{4+} to Ce^{3+} and oxidation of metallic Ca to Ca^{2+} . Upon heating to 600 K, large CaO nanofilms are observed on CeO_2 . Further increasing the temperature to 800 K, small CaO islands appear near the step edges and more Ca^{2+} ions migrate into the subsurface of CeO_2 . CO_2 adsorption on both stoichiometric CeO_2 and reduced CeO_{2-x} films at 180 K leads to the formation of surface carboxylate species. Moreover, the reduction of ceria enhances the CO_2 adsorption. On Ca-doped ceria films, CaCO_3 is identified on the surface. The presence of Ca^{2+} located on the ceria surface is observed to enhance the CO_2 adsorption.

References

- Huang, T. J.; Zhao, S. Y. *Appl. Catal. A* **2006**, 302, 325.
doi: 10.1016/j.apcata.2006.02.027
- Stacchiola, D. J. *Acc. Chem. Res.* **2015**, 48, 2151.
doi: 10.1021/acs.accounts.5b00200
- Rostrup-Nielsen, J. R. *Catal. Today* **1997**, 37, 225.
doi: 10.1016/S0920-5861(97)00016-3
- Wang, X.; Gorte, R. J. *Appl. Catal. A* **2002**, 224, 209.

- doi: 10.1016/S0926-860X(01)00783-9
- (5) Kong, D.; Zhu, J.; Ernst, K. H. *J. Phys. Chem. C* **2016**, *120*, 5980.
doi: 10.1021/acs.jpcc.5b10338
- (6) Hahn, K. R.; Iannuzzi, M.; Seitsonen, A. P.; Hutter, J. *J. Phys. Chem. C* **2013**, *117*, 1701. doi: 10.1021/jp309565u
- (7) Appel, L. G.; Eon, J. G.; Schmal, M. *Catal. Lett.* **1998**, *56*, 199.
doi: 10.1023/a:1019098121432
- (8) Jin, T.; Zhou, Y.; Mains, G. J.; White, J. M. *J. Phys. Chem.* **1987**, *91*, 5931. doi: 10.1021/j100307a023
- (9) Valenzuela, R. X.; Bueno, G.; Solbes, A.; Sapiña, F.; Martínez, E.; Cortés Corberán, V. *Top. Catal.* **2001**, *15*, 181.
doi: 10.1023/a:1016697615043
- (10) Pacchioni, G.; Ricart, J. M.; Illas, F. *J. Am. Chem. Soc.* **1994**, *116*, 10152. doi: 10.1021/ja00101a038
- (11) Kadossov, E.; Burghaus, U. *J. Phys. Chem. C* **2008**, *112*, 7390.
doi: 10.1021/jp800755q
- (12) Solis, B. H.; Cui, Y.; Weng, X.; Seifert, J.; Schauermaun, S.; Sauer, J.; Shaikhutdinov, S.; Freund, H. J. *J. Phys. Chem. Chem. Phys.* **2017**, *19*, 4231. doi: 10.1039/C6CP08504K
- (13) Kang, M.; Wu, X.; Zhang, J.; Zhao, N.; Wei, W.; Sun, Y. *RSC Adv.* **2014**, *4*, 5583. doi: 10.1039/c3ra45595e
- (14) Istadi; Amin, N. A. S. *J. Molec. Catal. A: Chem.* **2006**, *259*, 61.
doi: 10.1016/j.molcata.2006.06.003
- (15) Xu, Q.; Hu, S.; Cheng, D.; Feng, X.; Han, Y.; Zhu, J. *J. Chem. Phys.* **2012**, *136*, 154705. doi: 10.1063/1.4704676
- (16) Wang, W.; Hu, S.; Han, Y.; Pan, X.; Xu, Q.; Zhu, J. *Surf. Sci.* **2016**, *653*, 205. doi: 10.1016/j.susc.2016.07.007
- (17) Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baro, A. M. *Rev. Sci. Instrum.* **2007**, *78*, 013705.
doi: 10.1063/1.2432410
- (18) Lu, J. L.; Gao, H. J.; Shaikhutdinov, S.; Freund, H. J. *Surf. Sci.* **2006**, *600*, 5004. doi: 10.1016/j.susc.2006.08.023
- (19) Mullins, D. R.; Radulovic, P. V.; Overbury, S. H. *Surf. Sci.* **1999**, *429*, 186. doi: 10.1016/S0039-6028(99)00369-6
- (20) Fukui, K. I.; Namai, Y.; Iwasawa, Y. *Appl. Surf. Sci.* **2002**, *188*, 252.
doi: 10.1016/S0169-4332(01)00917-5
- (21) Hu, S.; Wang, Y.; Wang, W.; Han, Y.; Fan, Q.; Feng, X.; Xu, Q.; Zhu, J. *J. Phys. Chem. C* **2015**, *119*, 3579. doi: 10.1021/jp511691p
- (22) Campbell, C. T.; Peden, C. H. F. *Science* **2005**, *309*, 713.
doi: 10.1126/science.1113955
- (23) Mullins, D. R.; Overbury, S. H.; Huntley, D. R. *Surf. Sci.* **1998**, *409*, 307. doi: 10.1016/S0039-6028(98)00257-X
- (24) Pfau, A.; Schierbaum, K. D. *Surf. Sci.* **1994**, *321*, 71.
doi: 10.1016/0039-6028(94)90027-2
- (25) Skála, T.; Šutara, F.; Prince, K. C.; Matolín, V. *J. Electron Spectrosc. Relat. Phenom.* **2009**, *169*, 20. doi: 10.1016/j.elspec.2008.10.003
- (26) Skála, T.; Šutara, F.; Škoda, M.; Prince, K. C.; Matolín, V. *J. Phys.: Condens. Matter* **2009**, *21*, 055005.
doi: 10.1088/0953-8984/21/5/055005
- (27) Dupin, J. C.; Gonbeau, D.; Vinatier, P.; Levasseur, A. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1319. doi: 10.1039/a908800h
- (28) Li, S. Q.; Hu, J. S.; Liu, B.; Zhang, G. H.; Cao, W.; Wang, Q.; Zhang, N. *Cem. Concr. Res.* **1999**, *29*, 1549.
doi: 10.1016/S0008-8846(99)00111-8
- (29) Alba-Rubio, A. C.; Santamaría-González, J.; Mérida-Robles, J. M.; Moreno-Tost, R.; Martín-Alonso, D.; Jiménez-López, A.; Maireles-Torres, P. *Catal. Today* **2010**, *149*, 281.
doi: 10.1016/j.cattod.2009.06.024
- (30) Barin, I. *Thermochemical Data of Pure Substances*, 3rd ed.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2008; pp. 416–523.
- (31) Shao, X.; Myrach, P.; Nilius, N.; Freund, H. J. *J. Phys. Chem. C* **2011**, *115*, 8784. doi: 10.1021/jp201852x
- (32) Shao, X.; Nilius, N.; Freund, H. J. *J. Am. Chem. Soc.* **2012**, *134*, 2532. doi: 10.1021/ja211396t
- (33) Hu, S.; Wang, W.; Wang, Y.; Xu, Q.; Zhu, J. *J. Phys. Chem. C* **2015**, *119*, 18257. doi: 10.1021/acs.jpcc.5b04325
- (34) Skála, T.; Tsud, N.; Prince, K. C.; Matolín, V. *Appl. Surf. Sci.* **2011**, *257*, 3682. doi: 10.1016/j.apsusc.2010.11.107
- (35) Škoda, M.; Cabala, M.; Cháb, V.; Prince, K. C.; Sedláček, L.; Skála, T.; Šutara, F.; Matolín, V. *Appl. Surf. Sci.* **2008**, *254*, 4375.
doi: 10.1016/j.apsusc.2008.01.080
- (36) Ginting, E.; Hu, S.; Thorne, J. E.; Zhou, Y.; Zhu, J.; Zhou, J. *Appl. Surf. Sci.* **2013**, *283*, 1. doi: 10.1016/j.apsusc.2013.05.009
- (37) Vayssilov, G. N.; Lykhach, Y.; Migani, A.; Staudt, T.; Petrova, G. P.; Tsud, N.; Skála, T.; Bruix, A.; Illas, F.; Prince, K. C.; *et al.* *Nat. Mater.* **2011**, *10*, 310. doi: 10.1038/nmat2976
- (38) Skála, T.; Tsud, N.; Prince, K. C.; Matolín, V. *J. Phys.: Condens. Matter* **2011**, *23*, 215001. doi: 10.1088/0953-8984/23/21/215001
- (39) Staudt, T.; Lykhach, Y.; Tsud, N.; Skála, T.; Prince, K. C.; Matolín, V.; Libuda, J. *J. Phys. Chem. C* **2011**, *115*, 8716.
doi: 10.1021/jp200382y
- (40) Mudiyansele, K.; Senanayake, S. D.; Ferial, L.; Kundu, S.; Baber, A. E.; Graciani, J.; Vidal, A. B.; Agnoli, S.; Evans, J.; Chang, R. *Angew. Chem. Int. Ed.* **2013**, *52*, 5101. doi: 10.1002/anie.201210077
- (41) Doyle, C. S.; Kendelewicz, T.; Carrier, X.; Brown, G. E. *Surf. Rev. Lett.* **1999**, *06*, 1247. doi: 10.1142/s0218625x99001402
- (42) Lykhach, Y.; Staudt, T.; Streber, R.; Lorenz, M. P. A.; Bayer, A.; Steinrück, H. P.; Libuda, J. *Eur. Phys. J. B* **2010**, *75*, 89.
doi: 10.1140/epjb/e2010-00110-x
- (43) Hari, B.; Ding, X.; Guo, Y.; Deng, Y.; Wang, C.; Li, M.; Wang, Z. *Mater. Lett.* **2006**, *60*, 1515. doi: 10.1016/j.matlet.2005.11.062
- (44) Altrusaitis, J.; Usher, C. R.; Grassian, V. H. *Phys. Chem. Chem.*

- Phys.* **2007**, *9*, 3011. doi: 10.1039/b617697f
- (45) Kovačević, V.; Lučić, S.; Hace, D.; Packham, D.; Šmit, I. *Polym. Eng. Sci.* **1999**, *39*, 1433. doi: 10.1002/pen.11534
- (46) Voigts, F.; Bebensee, F.; Dahle, S.; Volgmann, K.; Maus-Friedrichs, W. *Surf. Sci.* **2009**, *603*, 40. doi: 10.1016/j.susc.2008.10.016
- (47) Fujimori, Y.; Zhao, X.; Shao, X.; Levchenko, S. V.; Nilius, N.; Sterrer, M.; Freund, H. J. *J. Phys. Chem. C* **2016**, *120*, 5565. doi: 10.1021/acs.jpcc.6b00433
- (48) Miao, S. *Appl. Surf. Sci.* **2003**, *220*, 298. doi: 10.1016/S0169-4332(03)00830-4
- (49) Ni, M.; Ratner, B. D. *Surf. Interface Anal.* **2008**, *40*, 1356. doi: 10.1002/sia.2904
- (50) Shui, M. *Appl. Surf. Sci.* **2003**, *220*, 359. doi: 10.1016/S0169-4332(03)00866-3
- (51) Staudt, T.; Lykhach, Y.; Tsud, N.; Skála, T.; Prince, K. C.; Matolín, V.; Libuda, J. *J. Catal.* **2010**, *275*, 181. doi: 10.1016/j.jcat.2010.07.032
- (52) Šutara, F.; Cabala, M.; Sedláček, L.; Skála, T.; Škoda, M.; Matolín, V.; Prince, K. C.; Cháb, V. *Thin Solid Films* **2008**, *516*, 6120. doi: 10.1016/j.tsf.2007.11.013
- (53) Matolín, V.; Cabala, M.; Cháb, V.; Matolínová, I.; Prince, K. C.; Škoda, M.; Šutara, F.; Skála, T.; Veltruská, K. *Surf. Interface Anal.* **2008**, *40*, 225. doi: 10.1002/sia.2625
- (54) Ochs, D.; Braun, B.; Maus-Friedrichs, W.; Kempter, V. *Surf. Sci.* **1998**, *417*, 406. doi: 10.1016/S0039-6028(98)00721-3
- (55) Vohs, J. M.; Barteau, M. A. *Surf. Sci.* **1988**, *201*, 481. doi: 10.1016/0039-6028(88)90499-2
- (56) von Niessen, W.; Bieri, G.; Åsbrink, L. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *21*, 175. doi: 10.1016/0368-2048(80)85046-8
- (57) Tegeler, E.; Kosuch, N.; Wiech, G.; Faessler, A. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 23. doi: 10.1016/0368-2048(80)80002-8