Revealing the Adsorption and Decomposition of EP-PTCDI on a Cerium Oxide Surface

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ABSTRACT: Cerium oxide has constantly attracted intense attention during the last decade both in research and industry as an appealing catalyst or a noninert support for catalysts, for instance, in the water-gas shift reaction and hydrogenation of the ketone group. Herein, the cerium oxide surface has been chosen to investigate the adsorption and decomposition behaviors of the N,N'-bis(1-ethyl-propyl)-perylene-3,4,9,10-tetracarboxdiimide (EP-PTCDI) molecule by photoelectron spectroscopy. As expected, EP-PTCDI molecules self-assemble on the cerium oxide surface comprising both trivalent and tetravalent cerium at room temperature. Interestingly, the EP-PTCDI molecule exhibits selective adsorption on cerium oxide after the heating treatment. It was found that the ketone group of EP-PTCDI first undergoes hydrogenation after annealing to 400 °C, which is probably related to the fact that high temperature annealing provides sufficient thermal energy to trigger the reaction between the ketone group and trivalent cerium. Furthermore, EP-PTCDI molecules are discovered to start to decompose hierarchically on the ceria substrate from annealing at 400 °C due to the strong molecule–substrate interaction and the effective catalysis by the trivalent cerium, whereas the decomposition sequence of functional groups is revealed to be, first, the ethyl propyl group (−C5H9), followed by the hydrogenated ketone (alcohols) group. Finally, our study may provide a new platform for the fundamental understanding of complex organic reactions on the cerium oxide surface.

INTRODUCTION

Cerium oxide (CeO2) has become a ubiquitous catalytic constituent in a wide range of applications such as photocatalysis, water-gas shift reaction, thermochemical water splitting, and organic reactions.1,2 For example, fuel cells with CeO2-based materials have almost entered into markets; meanwhile, ceria emerges as a novel material for other catalytic reactions, holding appealing promise for industrial applications in the future.3,4 Among these encouraging applications, one of the most attractive properties of cerium is the controllably converted chemical states between the trivalent (Ce(III)) and tetravalent (Ce(IV)) ceria, while Ce(III) is mostly perceived to be the active site for catalysis.5 Because of such convenient conversion, cerium or cerium-based structures can easily promote catalytic reaction by gaining or losing one electron. It has been widely accepted that because of the low redox potential between Ce(III) and Ce(IV), CeO2 usually dominates in the oxidative atmosphere; whereas in the reducing circumstances, Ce2O3 becomes predominant: CeO2 ⇌ CeO2−x + x/2O2. Accordingly, the cerium oxides can either provide oxygen for the oxidation or remove oxygen from the gas phase. The amounts of oxygen reversibly provided in and removed from the gas phase are called “oxygen storage capacities”.6 Consequently, under oxygen deficiency conditions such as ultrahigh vacuum (UHV), ceria oxide can easily release oxygen in the form of lattice oxygen, and oxygen vacancy is created accordingly. Nevertheless, varying oxygen vacancies can be created under different conditions which have already been reported experimentally before, for example, single surface oxygen vacancy and single subsurface oxygen vacancy are dominant when ceria is annealed at 900 °C for 1 min under UHV, whereas linear surface oxygen vacancy clusters are...

Received: March 13, 2019  
Accepted: May 31, 2019  
Published: October 25, 2019

DOI: 10.1021/acsomega.9b00696
ACS Omega 2019, 4, 17939−17946
dominant when ceria is annealed at 900 °C with longer annealing under UHV or other different annealing temperatures under UHV. Moreover, ordered vacancy clusters consisting of several oxygen vacancies were observed in the thin ceria film on Cu(111) after annealing to 527 °C under UHV, whereas ordered oxygen vacancy was obtained in one monolayer cerium film deposited on Rh(111) under an oxygen atmosphere at 527 °C annealing. Encouragingly, oxygen vacancies can reduce the potential barrier to facilitate on-surface reactions and, therefore, have different implications. For instance, the C−C coupling reaction is activated by oxygen vacancy dimers, the NO molecules can be converted into N₂ via the catalysis of surface vacancies.

In addition, oxygen vacancies have also been always utilized together with Ce(III) as the reaction center site. For example, cerium oxide has been used as the catalyst for the water-gas shift reaction (CO + H₂O → CO₂ + H₂), methanol synthesis (CO₂ + H₂ → CH₃OH), and carbon monoxide oxidation (CO + O₂ → CO₂) with the transformation between the Ce=O and C=O bonding during these reactions, which is considered to be associated with the participation of Ce(III). Nevertheless, such bonding conversion reported in literature occurs in the relatively small molecules or groups, and it is not yet clear whether the Ce=O/C−O bond from macromolecules with complex functions can be activated or not by Ce(III). On the other hand, the exploiting of adsorption and reaction mechanism of functional macrocycles/molecules on cerium oxide surface is relatively limited. In order to investigate the catalytic behavior of Ce(III) in complicated systems, herein, functionalized perylene tetracarboxylic diimide, namely, bis(1-ethylpropyl)-perylene-3,4,9,10-tetracarboxdiimide (EP-PTCDI, C₃₄H₂₆N₄O₄) has been chosen in this work, which comprises four C=O bonds and is shown in Scheme 1. As reported, this kind of molecules belonging to the class of perylene derivatives are versatile candidates toward organic optoelectronic applications due to their electronic, optical, and charge-transport properties, as well as the commercial availability and low cost. In practice, decomposition of the EP-PTCDI molecule has been explored on various substrates in literature reports, and it was figured out that the ketone (C=O) group was directly cleaved from the EP-PTCDI molecule, although the underlying mechanism has not been addressed yet. Based on these considerations, herein, we have comprehensively investigated the adsorption and decomposition behaviors of EP-PTCDI on cerium oxide as a function of molecular coverage and post-annealing temperature by X-ray photoelectron spectroscopy (XPS) and valence band spectroscopy. It is demonstrated that the interfacial interaction between EP-PTCDI molecules and the ceria substrate is related to molecular thickness. Furthermore, different parts in the EP-PTCDI molecule such as the perylene backbone or functional groups interact distinctly with the ceria substrate. Moreover, it has been revealed that the ketone group was first hydrogenated before decomposition, whereas the cracking of functional groups occurs at different elevated temperatures in sequence.

**RESULTS AND DISCUSSION**

As discussed before, cerium oxide is a good oxygen storage material; therefore, the cerium oxide foil might release oxygen under oxygen deficiency conditions, such as UHV or high-temperature annealing, tuning the oxidation state of ceria. Based on this consideration, XPS measurements of the sputtered cerium oxide foil are performed as a function of post-annealing temperatures which are illustrated in Figure 1. First, it is found from Figure 1a that the Ce 3d spectrum is rather complicated, where both tetravalent and trivalent components are observed. Surprisingly, there are in total five pairs of Ce 3d components resolved after peak fitting, of which three pairs belong to the tetravalent cerium and two belong to the trivalent cerium. In order to explain complex Ce 3d core level spectra, it has been proposed that the ground state of CeO₂ is in the mixed state of 4f⁰ and 4f¹L⁻¹ (L⁻¹ denotes a hole in the valence band), and three pairs of peaks are caused by screening effect of 4f electron with the O 2p orbital involved. Accordingly, final states of tetravalent cerium are Ce³d⁴f⁰O²p⁵, Ce³d⁴f¹O²p⁵, and Ce³d⁴f¹⁰O²p⁴. The paired components with the highest binding energy (BE) located at 917.1 and 898.6 eV, labeled as U¹ and V¹ in the Ce 3d spectrum, are related to the Ce³d⁴f⁰O²p⁵ final state, which is characteristic feature of the tetravalent cerium. Meanwhile, the paired components located at 908.0/889.4 eV are assigned to the Ce³d⁴f¹O²p⁵ final state marked with U²/V², and the U/V paired peaks located at 901.5/883.1 eV are, therefore, attributed to the Ce³d⁴f¹⁰O²p⁴ final state. Similarly, final states of trivalent cerium are Ce³d³⁴f¹⁰O²p⁶ and Ce³d⁴f¹⁰O²p⁵, in correspondence to the paired peaks located at 904.5 and 886.3 eV (U¹ and V¹) and the pairs located at 899.7 and 881.4 eV (U⁰ and V⁰). Herein, as revealed in Figure 1a for the foil after annealing to 100 °C in UHV, the tetravalent Ce 3d⁶/₂ and 3d⁵/₂ splitting pairs are located at 917.1/898.6, 908.0/889.4, and 901.5/883.1 eV of BE, whereas the trivalent Ce 3d splitting components are positioned with the BE at 904.5/886.3 and 899.7/881.4 eV. The coexistence of both tetravalent and trivalent cerium suggests the rich chemical states in the treated ceria foil with appealing applications in the surface catalysis field.

As the post-annealing temperature increases successively from 100 to 550 °C, the evolution of the tetravalent and trivalent cerium peaks has also been investigated and depicted in Figure 1b. For easy illustration, Ce 3d spectrum recorded at 100 and 460 °C annealing were selected and depicted in Figure 2a as a typical example. It is apparent from the Ce 3d spectrum on the top of Figure 1a that the tetravalent ceria has not completely transformed into trivalent cerium after annealing at 460 °C, retaining the mixed states comprising both trivalent and tetravalent ceria. However, the ratio of the trivalent and tetravalent cerium is increasing almost linearly as a function of annealing temperature according to the peak fitting analysis, say, from the initial 0.59 at 100 °C annealing to 1.22 after heated to 460 °C in UHV, as presented in Figure 1b, and the ratio of Ce(III) to Ce(IV) continually rises with elevating annealing temperature, which gets to 1.56 after heating to 550 °C.
The rising proportion of Ce(III) during annealing in UHV is probably induced by the reaction between the residual H2 gas from the UHV chamber and the ceria substrate, which partially transforms the Ce(IV) into Ce(III). In addition, the work function of the ceria foil after each heating treatment was calculated by measuring the exact position of the secondary cut-off in valence band spectroscopy, and the variation of work function is summarized in Figure 1b as well. Interestingly, the work function of the cerium oxide surface increases from 3.8 eV at beginning to 5.4 eV in the end, while the change is relatively big. At first sight, the increase of work function might be related to the increase of trivalent cerium on surface after thermal annealing: the more the trivalent cerium, the larger the work function, while the increment of both the trivalent cerium and surface work function is almost linear to the temperature elevation.

It is known that the 4f orbital of the trivalent cerium is partly occupied, splitting into two bands: one occupied orbital and another unoccupied orbital, whereas that of the tetravalent cerium is completely unoccupied. Consequently, the appearance and variation of trivalent cerium can be directly detected by monitoring the existence of occupied 4f orbital from the valence band structure.21,26 The monochromatic X-ray source ($h\nu = 1486.6$ eV) was utilized to measure valence band

Figure 1. Investigations on the ceria foil as a function of post-annealing temperatures in UHV. (a) Typical Ce 3d core levels recorded after annealing to 100 and 460 °C as examples. Raw data and fitted components are represented in different color; Ce(III) and Ce(IV) states are labeled as V0, V1 and V, V2, V3, respectively. (b) Work function variations of the cerium oxide foil as a function of post-annealing temperatures and the ratio changes between the trivalent and tetravalent cerium atoms. (c) Evolution of valence band structures of the ceria foil during thermal annealing taken with photon energy of 1486.6 eV.

Figure 2. In situ XPS investigations of Ce 3d, C 1s, and N 1s during sequential deposition of EP-PTCDI molecules. (a) Evolution of the Ce 3d core level at varying adsorption thickness. (b) Ratio variation of Ce(III)/Ce(IV) as a function of molecular film thickness. (c) Development of C 1s core-level spectra with increasing organic coverage. (d) Retaining of the N 1s spectrum during deposition. Raw data is plotted with dashed lines, while fitted components are displayed by colored solid curves.
structures, as the typical valence orbitals of heavy-metal elements is much more visible with high-energy photons as compared to ultraviolet photoemission spectroscopy. As expected, it is clear in Figure 1c that the intensity of the Ce 4f occupied state gradually increases with elevating annealing temperature, indicating the increase of the trivalent cerium. Additionally, we found a slight BE shift of the Ce 4f occupied state to a lower position as the percentage of trivalent cerium increases, that is, from 1.9 to 1.8 eV, which might be related to the change of work function of the cerium oxide substrate after annealing.

When EP-PTCDI was deposited on the ceria foil, uniform adsorption and growth of organic molecules can be recognized as judged from the sequential measurements of the Ce 3d core level in Figure 2a. First, the ratio of Ce(III)/Ce(IV) remains substantially during molecular deposition and adsorption. As can be clearly seen, the ratio is 1.56 before adsorption, and substantially during molecular deposition and adsorption. As judged from the sequential measurements of the Ce 3d core level in Figure 2a, the ratio of Ce(III)/Ce(IV) remains substantially during molecular deposition and adsorption. As can be clearly seen, the ratio is 1.56 before adsorption, and substantially during molecular deposition and adsorption.

Figure 3. Core-level investigations of cerium, carbon, and nitrogen during heating treatment after molecular adsorption. (a) Evolution of Ce 3d core levels from 100 to 500 °C. (b) Ratio variation of Ce(III)/Ce(IV) as a function of annealing temperature. (c) Changes of the C 1s spectra during critical annealing steps. (d) Variation of the N 1s core levels in sequential annealing.

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around 4.0 Å) was treated by post-annealing in sequence from 100 to 500 °C. It can be recognized from the Ce 3d spectra that no obvious change was induced with annealing below 300 °C except the decline of peak intensity due to molecular desorption after thermal annealing. However, visible changes are found in the Ce 3d spectrum when the annealing temperature reaches 300 °C. First, the ratio of Ce(III)/Ce(IV) changes dramatically, as shown in Figure 3b. The ratio of Ce(III) to Ce(IV) atoms first goes up sharply to 6.5 at 300 °C annealing, gradually drops slowly to 5.6 after annealing to 400 °C, followed by a considerable decrease to about 3 when annealed at 500 °C. Interestingly, the characteristic tetravalent paired components (Ce 3d5/2 and 3d3/2) originally positioned at 917.1 and 898.6 eV disappear after annealing to 300 °C, and recover until 500 °C annealing. The disappearance of the paired components does not say that the tetravalent cerium is completely gone because the other two pairs of Ce(IV) component are still apparent. However, the fine electronic structure of the tetravalent cerium has been apparently modified within the annealing temperature range between 300 and 500 °C. As discussed, the paired 3d5/2 and 3d3/2 peaks located at 917.1 and 898.6 eV are the typical features of the tetravalent cerium embedded with the Ce3d4f6O2p6 orbital structure. Triggered by high-temperature annealing, on-surface reaction of cerium oxide with the residual H2 from the UHV chamber might happen without too much difficulty and the Ce3d4f6O2p6 hybridized orbital can be changed into Ce3d4f5O2p6 by gaining one electron, resulting in partial transformation from tetravalent to trivalent cerium, which is in agreement with the observations on the pristine CeO2 substrate mentioned earlier and the previous report of CO molecules reacted on CeO2.35,36 The drop of the proportion of Ce(III) and the recovery of characteristic Ce(IV) ions at annealing to 500 °C, may suggest the active involvement of Ce(III) in the on-surface reaction between EP-PTCDI molecules and substrate.

Elaborate investigation of the C 1s spectra during annealing might provide more insight into the on-surface reaction mechanism. It is discovered that the shape of C 1s core level signal is well preserved during annealing until 300 °C. Interestingly, as seen in Figure 3c, the peak located at 289.0 eV disappears after annealing to 400 °C, indicating the vanishing of C=O double bonding. Meanwhile, the component at 286.8 eV gets much stronger. As the N-bonded carbon cannot apparently increase, the visible spectrum change at 286.8 eV can be assigned to formation of the single C–O bond with the alcohols group, which has a similar BE to the nitrogen-bonded carbon and is probably induced by the hydrogenation of the original C=O bond assisted by the catalysis of the trivalent cerium [Ce(III) is consequently converted into Ce(IV) after hydrogenation], in agreement with the slight proportion drop of Ce(III) after annealing to 400 °C. Furthermore, only the main sp2/sp3 component is retained after annealing to 500 °C, it is therefore expected that only the perylene backbone of the EP-PTCDI molecule is left on the oxide surface. Besides changes of C 1s spectra during step-by-step thermal annealing of the adsorption complex, fascinating variations have also been revealed in N 1s core level spectra. Similar to the C 1s spectra, no visible change among the N 1s spectra is found when the annealing temperature is below 400 °C. However, as the annealing temperature is further increased to 400 °C, a new peak appears at the BE of 399.3 eV in the N 1s spectrum, which shall be connected to the metal-bounded nitrogen.39 Therefore, we can infer that nitrogen atoms strongly interact with the cerium atoms underneath, indicating that the ethyl propyl (EP) functional group begins to cleavage after thermal annealing is promoted to 300 °C while no visible change was discovered. (c) Further annealing to 400 °C, resulting in the cleavage of the EP functional group and hydrogenation of the ketone group. (d) After annealing to 500 °C, all groups are detached from the molecule.

Figure 4. A schematic diagram illustrating the adsorption and on-surface reaction of EP-PTCDI on the ceria substrate during post-thermal annealing. (a) Adsorption of EP-PTCDI on CeO2 at RT. (b) Organic/ceria complex was heated to 300 °C while no visible change was discovered. (c) Further annealing to 400 °C, resulting in the cleavage of the EP functional group and hydrogenation of the ketone group. (d) After annealing to 500 °C, all groups are detached from the molecule.
2.8 to 6.5, with the characteristic feature of Ce(IV) removal. At the same time, no visible change of C 1s or N 1s has been witnessed yet. Subsequently, once the annealing temperature gets to 400 °C, the cleavage of the EP functional group is triggered with partial detachment, whereas hydrogenation of the carbonyl group into the alcohols group happens as well, both of which are expected to be assisted by the trivalent ceria.13 Surprisingly, the proportion of trivalent cerium was found to drop back when the annealing temperature reaches 500 °C, which means the Ce(III) atoms greatly participate in the on-surface reaction, for instance, cleavage of the alcohols functional group. As known, Ce(III) is converted into Ce(IV) because of the interaction between the residual nitrogen and cerium atoms on the surface, as discovered in the N 1s spectrum in Figure 3d with the metal-bounded N. Consequently, the ratio of Ce(III)/Ce(IV) returns to the initial value. Interestingly, metal-bounded nitrogen atoms are robustly adsorbed on the oxide surface after the decomposition of molecule, indicating a strong N—Ce bonding/interaction, whereas only the perylene backbone is left on surface. For easy illustration, the on-surface adsorption and reaction mechanism of P-PTCDI on CeO$_2$ surface has been summarized in a cartoon diagram and presented in Figure 4.

### CONCLUSIONS

We have comprehensively investigated the adsorption and on-surface reaction of the EP-PTCDI molecule adsorbed on a ceria foil and demonstrated the robust thermal stability of EP-PTCDI on the CeO$_2$ substrate. To start with, sole heating treatment was applied to the CeO$_2$ foil to check the variation of trivalent cerium, which is expected to be the active center for catalysis. It was found that the proportion of trivalent cerium increases together with the work function of the foil as a function of annealing temperatures, implying the occurrence of on-surface reaction. Thereafter, EP-PTCDI molecules are deposited onto the ceria oxide substrate kept at room temperature, where weak molecule—substrate interaction is revealed. Followed by sequential thermal annealing, it is surprisingly discovered that the EP-PTCDI molecule is stably adsorbed on the CeO$_2$ foil until annealed to 400 °C, while the ratio of Ce(III)/Ce(IV) increases sharply at annealing to 300 °C. Interestingly, the EP group starts to detach from molecules, and the carbonyl group undergoes hydrogenation by the catalysis of the trivalent cerium after 400 °C heating. As expected, the interaction between functional groups and cerium is much stronger than that between the perylene backbone and substrate. As the annealing temperature rises to 500 °C, it is inferred that the perylene backbone is left on the surface, which might be further transformed into other carbon-based species via cross linking, together with the Ce-bounded nitrogen atoms detached from EP-PTCDI. In the end, our report provides new insights toward the explicit understanding of surface/interface reactions in the CeO$_2$ system widely utilized in catalysis.

### EXPERIMENTAL METHODS

XPS measurements were carried out with a SPECS PHOIBOS 100 spectrometer using a monochromatic Al Kα source ($h\nu = 1486.6$ eV). The base pressure in the vacuum chamber was maintained better than $1.0 \times 10^{-7}$ mbar throughout the whole measurement. Work function of the analyzer was calibrated to give the Au 4f$_{7/2}$ core level a BE of 84.1 eV. High-resolution spectra were obtained by choosing a $3 \times 7$ mm$^2$ spot size and the pass energy of 10 eV, resulting in the full width at half maximum of 0.2 eV in the Au 4f$_{7/2}$ spectrum.

The cerium foil was purchased from Sigma-Aldrich with a purity of 99.9%, while the oxidized cerium was obtained by gradual oxidation in air on purpose. Before loading into the UHV chamber, it was first polished in alcohol with fine sandpaper followed by ultrasonic cleaning for 20 min in ethanol and acetone, respectively. In order to remove surface impurity and contamination, the oxide foil was further cleaned by argon sputtering in the UHV chamber with an ion energy of 1.0 k eV for 8 h, and the cleanness of the foil was checked by XPS. Interestingly, there is a very tiny and negligible carbon impurity with the peak position located at 285.4 eV, which cannot be completely removed from the surface, and is most probably related to the intrinsic impurity from the ceria bulk. Deposition of EP-PTCDI molecules was carried out in situ in the XPS chamber, and the coverage was monitored by a quartz microbalance and double checked by evaluating the intensity attenuation of Ce 3d peak in core level spectra. Post-annealing of the ceria foil was performed in sequence with each step having the duration of half an hour.

XPS peaks were fitted afterwards utilizing the XPSPEAK software. During the fitting process, the Lorentzian—Gaussian ratio of paired peaks was kept at a constant value, the same as that for the peak area; for example, the peak intensity ratio of Ce 3d$_{5/2}$ and 3d$_{3/2}$ components is set to 1.5 according to the spin-orbital splitting of Ce 3d. In addition, difference in peak positions of paired peaks was also kept to a fixed value in accordance with the XPS database.$^{30,44}$ Afterwards, proportions of chemically different cerium atoms can be precisely evaluated by comparing the peak area of the trivalent and tetravalent cerium.$^{32,43}$

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

Discussions with Prof. Dr. Xingyu Gao are greatly appreciated. This work is financially supported by the National Natural Science Foundation of China (11874380, U1732267) and National Key Research and Development Program of China (2016YFA0401302).

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