Evaluation and X-Ray Induced Modification of the Cerium Oxidation State in Cerium Calixarene Complexes

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Abstract. The cerium oxidation state in novel calixarene-supported cerium(IV) $\beta$-diketonate complexes [$p$-$^3$Bu-calix[4](OMe)$_2$(O)$_2$]Ce(acac)$_2$ (1) and [$p$-$^3$Bu-calix[4](OMe)$_2$(O)$_2$]Ce(hfac)$_2$ (2), which are a new class of potential precursors for homogeneous oxidative transformations, has been determined using X-ray photoelectron spectroscopy (XPS). Cerium oxidation states between 3.6 and 3.65 were detected, distinctly different from their nominal value of $+4$. An X-ray induced photoreduction of these compounds was detected. Because of the observed stability of the X-ray modified oxidation state under ambient conditions this effect might be used for a long-standing fine tuning of the Ce oxidation state in cerium calixarenes.

Introduction

Cerium oxide compounds are efficiently used in heterogeneous oxidation catalysis due to the ability of Ce atoms to easily change their ionic charge and thus vary the Ce oxidation state $\text{Ce}_{\text{ox}}$ (see e.g. [1,2]). This feature makes the cerium oxide containing compounds interesting for other applications, such as e.g. oxygen storage materials and Ce-doped copper oxide superconductors [3], solar cells [4], solid oxide fuel cells [5], buffer layers for YBCO high-temperature superconductors [6,7], gates for metal-oxide semiconductor devices or phosphors [8-10]. It can be anticipated that the Ce-based complexes will be technologically important for applications such as homogenous catalysis or for CVD processes. Their oxidation state is a topic of intensive discussions, particularly as some unexpected results have been obtained. For example, in the double-decker tetrapyrrole cerium complexes, the XANES (X-ray absorption near edge structure) and XPS (X-ray photoelectron spectroscopy) studies of [Ce(Pc)$_2$] (Pc = phthalocyaninate) detected a partial delocalization of the ligand $\pi$-electrons into a cerium 4f orbital resulting in a valency that is neither $+3$ nor $+4$ [11], while in Ce(IV)-COT (COT = cyclooctatetraenyl) and substituted -COT complexes [12-14], the Ce oxidation state was found to be close to $+3$ by means of studies of their magnetic properties [15] and XANES experiments [16], as well as on the basis of theoretical considerations [17]. In both cases this is contrary to expectations, which would suggest an oxidation state of $+4$.

Unfortunately, the determination of $\text{Ce}_{\text{ox}}$ by a standard technique such as XPS is difficult, mainly due to the variable occupancy of the Ce 4f level; the redistribution of the levels is caused by the core hole creation and changed hybridization at different oxidation states [18,19]. This leads to complex features in the Ce 3d X-ray photoelectron (XP) spectra. As a result, their interpretation is not always unambiguous and sometimes even contradictory [20]. Artifacts created merely by the X-ray exposure during the XPS measurements might also cause additional difficulties [21].

Two novel complexes with cerium-oxygen bonds and the potential for homogeneous oxidative transformation catalysis, namely the calixarene-supported cerium(IV) $\beta$-diketonate complexes [$p$-
\(^{1}\)Bu-calix[4](OMe)\(_2\)(O\(_2\)Ce(acac)\(_2\)) (1) and \([p^{3}\text{-Bu-calix[4](OMe)\(_2\)(O\(_2\)Ce(hfac)\(_2\)]})\) (2), were recently synthesized in an equimolar reaction between \(p^{3}\text{-Bu-calix[4](OMe)\(_2\)(OH)\(_2\)}\) with Ce(acac)\(_4\) (acac = acetylacetonate) and Ce(hfac)\(_4\) (hfac = 1,1,5,5,5-hexafluoro-acetylacetone), respectively [22,23]. Since the expected catalytic activity of these compounds should be closely related to their Ce valency, it is interesting and important from the aspect of basic and practical considerations to evaluate their Ce ionic charge. In the present contribution the Ce oxidation state in the model compounds 1 and 2 was evaluated using XPS. An X-ray-induced photoreduction of the Ce centre in 1 and 2 which may make oxidation state fine-tuning possible is also reported.

**Experimental**

The synthesis of the model compounds 1 and 2 was carried out in an inert atmosphere of dry nitrogen using the standard dry box and Schlenk techniques. The details of the synthesis and the derivation of the molecular structure for 1 and 2 by single crystal X-ray determination are published elsewhere [22 - 25].

X-ray photoelectron spectra were obtained from the dry powders of 1 and 2, which were carefully ground and fixed to Mo sample plates under an argon atmosphere in a glove box and transferred under inert gas to UHV multipurpose surface analysis apparatus (SPECS, Germany). To avoid a vacuum-induced reduction of the samples [26], a “fast transfer” XPS mode was used: the load-lock and transfer systems allow sample-transfer times of less than 5 min between the start of the evacuation of the load lock and the first XPS spectrum at a pressure better than \(5 \times 10^{-9}\) mbar. A monochromatized X-ray source (FOCUS 500, SPECS, excitation energy 1253.74 eV, Al-K\(_\alpha\), linewidth < 0.3 eV) was used. High-resolution spectra (pass energy 10 eV, step size 0.1-0.2 eV) were recorded at room temperature with a hemispherical energy analyzer (PHOIBOS 150, SPECS) with simultaneous photo-electron detection on 9 channels and fast data acquisition times (0.5 s per data point) with a satisfactory signal-to-noise ratio. No charge compensation was used in the experiments and the correction for static charging was performed by assigning a value of 284.5 eV to the C 1s peak of adventitious carbon.

**Results and discussion**

**Calibration of reference samples.** The direct use of established techniques, such as the commonly used deconvolution of high-resolution XP spectra, to evaluate the Ce oxidation state in coordination compounds is still difficult despite the great deal of work devoted to the electronic structure of ceria and similar compounds [18-20,27,28]. As already mentioned, the major difficulties result from the particular features in the Ce 3d XP spectra which are related to the multielectronic processes caused by the f-character of the O 2p valence electrons (the initial state effect) and to a screening effect of the core-holes left by photo-emitted electrons (the final state effect) [29,30]. This results in an extremely complicated spectrum with overlapping peaks when both oxidation states (Ce\(^{3+}\) and Ce\(^{4+}\)) are present. Despite an extensive theoretical effort [31,32] some inconsistency in the interpretation of the Ce 3d spectra remains. In particular, the necessity to consider a total of 30 parameters, including the peak position, relative peak intensity and the FWHM for each of 10 peaks presented in Ce 3d spectra, makes it difficult to get a consistent and unique evaluation of the entire spectrum [33]. Even such a sophisticated procedure as factor analysis, a method successfully applied to other spectroscopic problems, meets its limits in the case of Ce 3d spectra evaluation [27].

In this work the effective oxidation state of Ce in cerium calixarene complexes by correlation of the XPS data for the studied samples 1 and 2 with those for reference samples CeO\(_2\)\(_{2-x}\) with a known oxidation state was obtained. As reference samples Ar\(^{+}\)-sputtered CeO\(_2\) was used, where the preferential release of oxygen atoms in the surface region due to the impact of Ar\(^{+}\) ions in ultrahigh
vacuum (UHV) leads to deviations from the ideal bulk stoichiometry in the top surface layers. This leads to the reduction of Ce$^{4+}$ to Ce$^{3+}$ ions and permits the creation of CeO$_{2-x}$ surface oxides with continuously variable effective oxidation cerium states Ce$_{ox}$ in the range from 4 to 3.4. The formation of a certain depth distribution of Ce$_{ox}$ within the topmost layers of the sample should not influence the evaluation since the information depth from the Ce 3d and O 1s photoelectrons does not differ significantly. A similar method, proposed earlier by Coulston et al. [34], has recently been applied for the determination of the oxidation state of vanadium in vanadium oxide and vanadium phosphorus oxide catalysts [26]. In order to avoid X-ray induced damage of the CeO$_2$ sample, the X-rays were applied in a “gentle” way by limiting the operation power (< 180 W) of the monochromatic X-ray source, which, in addition, was switched on only during the data acquisition. In Fig. 1 two typical Ce 3d XP spectra of “fresh” CeO$_2$ as introduced to UHV (front spectrum) and after a prolonged Ar$^+$ sputtering (rear spectrum) are presented.

![Ce 3d XP spectra of CeO$_2$](image)

In Table 1 the meaning of the indicators used in Fig. 1 as well as details of the initial and the final states caused by electron transitions from the valence band into Ce 4f states are summarized [18].

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<th>Ion</th>
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<td>Ce$^{3+}$</td>
<td>$3d^{10}$ $f^8$</td>
<td>$u_1; u_2; 3d^9f^8 4f^{n-1}$</td>
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<td>$3d^{10}$ $f^8$</td>
<td>$u_1; u_2; 3d^9f^8 4f^n$</td>
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<tr>
<td>Ce$^{4+}$</td>
<td>$3d^{10} f^9$</td>
<td>$v_0; v_1; 3d^9f^9 4f^{n-2}$</td>
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V denotes the valence band; $v_i$ and $u_i$ ($i=0;1;2$) correspond to intensities of Ce$^{4+}$ and Ce$^{3+}$ states, respectively. Components $v_i$ and $u_i$ are attributed to Ce 3d$_{5/2}$ contribution and $v'_i$ and $u'_i$ to the Ce 3d$_{3/2}$ contribution, correspondingly.

Table 1. Initial and final states of Ce$^{4+}$ and Ce$^{3+}$ ions in Ce 3d core level XP spectra (based on Ref. [18], but using the indexing $v_i$ and 18], but using the indexing $v_i$ and $u_i$ of individual peaks as proposed in Ref. [35]).

**Determination of the cerium oxidation state in the calixarene complexes.** The XPS measurements performed on the cerium calixarene complexes 1 and 2 provide distinct peaks in the Ce3d spectra, however, the determination of Ce$_{ox}$ has to be done in a careful manner because an X-ray induced photoreduction of samples of both compounds studied was detected. This effect, which can adulterate the results of the XPS measurements, is in principle known, but not entirely understood, for some materials containing rare earth elements such as Sm$^{3+}$-doped fluoroaluminate glasses or the pure CeO$_2$ [36,37]. The rear spectrum in Fig. 2a, recorded after 380 min of constant X-ray irradiation of compound 1, differs clearly from the previous spectrum, registered just after the fast transfer from the inert dry N$_2$ environment to UHV. Similar changes were observed for
compound 2 (Fig.2b) when compared to the initial (front) spectrum and with the rear one, recorded 340 min later.

**Fig. 2:** (a) X-ray induced evolution of the 3d-region of the XP spectra for complex 1. Front: initial state spectrum. Rear: spectrum after exposure to X-rays for 380 min. Positions of individual peaks are the same as in Fig. 1. Peak distances are given in eV. (b) The same for complex 2 (340 min exposure).

Thorough long-time studies of the dynamical response of the Ce oxidation state to the X-ray irradiation revealed an exponential decay of Ce$_{ox}$ with irradiation time (Figs. 3a, b) where the extrapolation to zero exposure facilitates the determination of the initial oxidation state in the freshly synthesized compounds to 3.61±0.18 for 1 and 3.65±0.18 for 2, respectively.

**Fig. 3:** (a) Time dependency of the average Ce oxidation state Ce$_{ox}$ for complex 1 under constant X-ray irradiation. Extrapolation to “zero irradiation” provides the initial values of Ce$_{ox}$. (b) The same for complex 2.

It has to be noted that in contrast to vanadium-containing oxide compounds no UHV-induced modification of the cerium oxidation state has been observed in the present study, i.e. the observed effect is a purely X-ray induced photoreduction. The X-ray modified oxidation state of cerium remained stable after exposure of the samples to air at room temperature. This means that a fine tuning of Ce$_{ox}$ in the range 3.60 – 3.28 for 1 (3.62 - 3.27 for 2) is in principle possible, depending on the X-ray dosing. Under this aspect, it should also be noted that the attenuation length of the Al K$_\alpha$ photons exceeds the XPS information depth of ≈ 2.5 nm by at least three orders of magnitude in the present case. Therefore, the irradiation-caused changes in the Ce oxidation state may extend to a significant depth, exceeding the thickness of any catalytically active layer (≤ 5 nm).
Concerning the possible interpretation of the observed photoreduction effect, it was noted that a strong controversy exists in the literature concerning the interpretation of the photoreduction effect observed for ceria: at least three different mechanisms are proposed [37-41]. However, experimental proof of particular assumptions as well as a theoretical substantiation is still missing. In this case of calixarene compounds, the authors were able to test at least two of the suggested explanations: Firstly, the local irradiation-induced heating proposed as a reduction mechanism for ceria [37] cannot explain the present observation since no significant increase of the surface temperature was observed and, secondly, another possible mechanism is associated with an impact of the numerous low-energy electrons which could cause desorption due to their large cross-section [40, 41]. This, however, seems to be less probable in the present case as was proven in situ by low-energy electron bombardment from an external electron gun. A decomposition of the compounds due to an X-ray damage of the ligands could also be suggested, however, this was not observed in the long-standing structural determination by single crystal X-ray diffraction with an X-ray exposure over more than 24 h [22]. Apparently alternative mechanisms such as electron-hole pair formation and Auger decay which are favoured for ceria [38] and for aluminovanadate oxides [39] must be taken into particular account. To prove entirely the latter mechanism, additional experimental and theoretical effort is necessary.

Conclusions

The first evaluation of the Ce oxidation state in novel cerium calixarene complexes with XPS is reported. X-ray irradiation of the studied samples causes a photoreduction with an exponential decay of $\text{Ce}_{\text{ox}}$ with the irradiation time. The extrapolation to zero exposure allows the determination of the initial oxidation state in the freshly synthesized compounds, which lies between 3.6 and 3.65 for both and differs from the expected cerium oxidation state of +4. The stability of the photoreduced samples under ambient conditions suggests the possibility of an oxidation state fine-tuning of cerium in the studied compounds. Electron-hole pair formation and Auger decay are favoured as mechanisms for the observed X-ray induced photoreduction on the basis of the experimental observations.

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References


[24] Crystallographic data for the structure of (1) have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication 271677.

[25] Crystallographic data for the structure of (2) have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication 616674.


