4514 *Chem. Mater.* **2010,** *22,* 4514–4516
DOI:10.1021/cm100735n

CHEMISTRY OF
MATERIALS
Comment

Comment on "Novel Nanocrystalline $Ce_{1-x}La_xO_{2-\delta}$ ($x = 0.2$) Solid Solutions: Structural Characteristics and Catalytic Performance"

In a recent paper,[1] Reddy et al. reported on the catalytic properties of ceria−lanthana (CeO_2−La_2O_3) solid solutions (hereafter CL) using a number of analytical methods, and here I shall comment on the XPS analysis described in that paper. Knowledge of the surface composition is essential for a better understanding of the chemical properties of catalysts, and XPS[2] is a most suitable means for studying them, as it possesses the capacity both to probe the outermost regions of solids (say 1−3 nm) and to map the oxidation state of the elements sitting there, particularly the oxidation state(s) of cerium ions in CL solid solutions. Hence, XPS analysis of these materials is of paramount importance in elucidating their catalytic properties, but I find that the interpretation offered in the paper by Reddy et al. is largely unwarranted.

Detailed theoretical studies show that the ground state of CeO_2 is a "mixed valence state" involving contributions from $4f^0$ and $4f^1$ configurations which populate the 4f level with an average electron occupancy $n_f \sim 0.5$.[3,4] Reddy et al. maintain that the XPS Ce3d spectra which they show in Figure 2 "are complex due to spin-orbit coupling". In fact, the main complexity arises not from spin−orbit splitting, which partitions photoemitted Ce3d electrons into 5/2 and 3/2 components, but from electron correlation (mainly final-state) effects which produce as many as six peaks, spread over a ~35 eV interval. The two lower binding energy (BE) peaks for each of the 5/2 and 3/2 components arise from final states in which $4f^1$ and $4f^2$ configurations are strongly mixed, whereas the contribution peaked with the highest BE, at ~898 eV (5/2 component) and 916.5 eV (3/2 component), arise from the almost pure $4f^0$ final state.[3] There had been in the past conflicting claims (both theoretical and experimental) whether—as well as these six peaks—a peak denoted v′, lying at BE ~ 885 eV, and a peak denoted *u*′ at BE ~ 904 eV also belong to the photoemission Ce3d spectrum of CeO_2.[3,5−11] As early as 1978, Barr[6] noted that the position of peak v′ is very close to that of the most intense peak of the Ce3d spectrum of Ce_2O_3, thus implying a possible chemical reduction of Ce^{4+} ions to Ce^{3+} ions. Barr's observation prompted a subsequent detailed verification of this possibility, and the controversial signals v′ and *u*′ were definitely demonstrated to arise from Ce_2O_3-like species, which formed as a result of prolonged X-ray irradiation of the ceria surface during XPS measurements.[12,13] Indeed, the XPS Ce3d spectrum of Ce_2O_3 contains a total of four peaks,[5,6,9,12,13] specifically a doublet for each of the two spin−orbit components, the maxima of which fall at BE = 885.3 ± 0.5 eV (component 5/2) and at 903.8 ± 0.5 eV (component 3/2), that is, merely the same locations of the v′ and u′ peaks, respectively. In other words, peaks v′ and u′ are *not* the manifestation of an electron correlation interaction involved in the final state left behind photoionization of Ce3d electrons of CeO_2, but of the chemical reduction of this oxide to Ce_2O_3-like oxide arising from prolonged exposure of the starting surface to X-ray irradiation during XPS experiments.

There are some aspects of Reddy et al.'s interpretation of the spectra in Figure 2 which I find very difficult to reconcile with the theoretical, experimental, and methodological state of affairs of the XPS Ce3d spectra of cerium oxides:

(i) BE values of Ce3d peaks given by Reddy et al. (see also Table 2) may differ by up to 1−1.5 eV from those by other workers.[6,12,13] Such a difference is likely to arise from the fact that the latter based their confidence in the linearity of the energy scale of their spectrometer by calibrating it against well-known BE values of core-level transitions of reference materials, such as $Au4f_{7/2}$, $Cu2p_{3/2}$, and so forth,[14] which both cover an interval as wide as ~850 eV and include the BE region of the Ce3d spectrum. By way of contrast, the linearity of the energy scale involved in Reddy et al.'s experiments seems to rely only on the assumption that the BE of the C1s = 284.6 eV, a procedure that is expected to grant a comparatively poor linearity of the energy scale because this peak lies as much as ~600 eV apart from the Ce3d peaks. (I shall discuss specific results concerned with charging phenomena and BE scale calibration in a subsequent part of my comment).

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(ii) Second, the presence of relatively intense peaks v′ and u′ in the reference spectrum from the starting ceria sample (C) indicates that even the surface of this material (which the authors use as the spectral signature of pure CeO_2) contains a sizable amount of Ce_2O_3 oxide.[6,12,13]

(iii) Third, unlike the authors' claim,[1] the spectra of the CL solid solutions, including the intensity of Ce^{3+}-related peaks v′ and u′, change meaningfully neither with respect to that of pure ceria nor as a function of temperature. Note that the spectrum of ceria is scaled to a lower size both vertically and horizontally, but a careful inspection shows that its profile is much the same as that of all the other spectra collected in Figure 2. Also note that the spectrum of sample CL heated at 1073 K is not normalized on the vertical axis to the spectra recorded at lower temperatures, but it is scaled down by a factor ∼1.4, and this is particularly also the case for the peak at BE ∼ 916.5 eV, usually denoted u‴, which is an indicator of CeO_2 species.[6,12,13] As a consequence, once the scaling factor is allowed for, one is forced to conclude that even the surface CeO_2/Ce_2O_3 site ratio producing this spectrum is not significantly different from those producing the remaining spectra. Generally speaking, when all the spectra of Figure 2 are consistently compared with one another, changes would be found neither in the "valley" (to use Reddy et al.'s terminology)[1] depth in between peaks v and v′ and u and u′, nor in the intensity of peak u‴. In reality, the spectral changes, if any, induced by the mixing of CeO_2 with La_2O_3 as a function of temperature are lower than, and therefore masked by, the well-known X-ray irradiation induced effects, that is, the chemical reduction of CeO_2 to Ce_2O_3-like species, which proves the dominating reason for the apparent profile of the Ce3d spectra in Figure 2. This methodological aspect is completely ignored by the authors, if not for their short and vague remark that "the conversion of $Ce^{4+} \rightarrow Ce^{3+}$ is possible under the vacuum in agreement with the earlier reports".[1] These "earlier reports" do in fact mention that the conversion is caused by X-ray irradiation,[15] whereas it is well established that CeO_2 surfaces remain chemically stable in UHV conditions up to temperatures as high as ∼900 K.[10]

I find largely unwarranted even the interpretation of the results shown in Figure 3, which the authors refer to as the XPS Ce4d spectra recorded on the CL samples. Note that on the high BE side all the spectra are truncated at ∼125 eV, an arbitrary choice which keeps off some of the 5/2;3/2 spin−orbit split signals originating from photoionization of Ce4d electrons.[5,6,12,13]

The spectra contain a well visible, if broad, band at ∼103 eV which the authors interpret as arising from trivalent cerium species, as "the band at ∼103.3 eV" they say "is directly correlated to the proportion of Ce^{3+} component,"[1] and from this they conclude that its presence shows that both Ce^{4+} and Ce^{3+} oxidic species coexist at the surface of their CL solid solutions. True, such a band is expected to occur in the photoemission Ce4d spectra of Ce_2O_3-bearing materials, but this holds true only for cases which differ in three important respects from that at hand in Reddy et al.'s paper:

(i) Its intensity is quite low with respect to that of the leading Ce4d band,[6] (ii) it is expected to be observed in photoemission experiments conducted on surfaces which involve the cerium totally and exclusively in the trivalent state,[6,16] and (iii) its presence can be ascertained only if the spectra are recorded with a sufficiently high energy resolution, as that available in XPS spectrometers equipped with a monochromated Al Kα source[6] or, even better, in synchrotron radiation photoemission experiments.[16] None of conditions (i) through (iii) is met in the experiments described by Reddy et al. because their allegedly Ce^{3+}-related signal is observed on surfaces which invariably contain a major contribution from CeO_2 species, in the presence of which the weak, genuine Ce^{3+}-related signal at ∼103 eV is hardly seen with the comparatively poor energy resolution available with their XPS spectrometer (Shimadzu ESCA 3400). Indeed, contary to the aurhors' claim, the latter is equipped with a *nonmonochromated* Mg Kα source.[17] Moreover, this signal cannot be interpreted as arising from Ce^{3+} species because, relatively speaking, its intensity is not low at all, but as high as about half that of the leading Ce4d band, and it overlaps massively with it. The only assignment which reasonably accounts for the spectra in Figure 3 is that the broad, intense signal at ∼103 eV arises from the La 4d transition (precisely, the low BE part of the 5/2;3/2 doublet) from the La_2O_3 oxide,[6,18] which is one of the components of the solid solutions studied by Reddy et al.[1] (I should anticipate that no such signal would be visible in the Ce4d spectrum of pure ceria, but—unlike Figure 2—unfortunately no such spectrum is shown here.) This assignment is further corroborated by the fact that the intensities of the Ce4d and La4d signals[19] seem consistent with the [Ce]/[La] atomic ratios measured for these CL solutions.[1]

The BEs the authors measured at the maximum of the leading, lattice-component in O1s spectra, and the Ce3d (u‴) component of CeO_2 (Table 2), also invite reservations concerning accuracy and consistency. The O1s results may vary by more than 1 eV from each other and on the whole they are, as I have already recalled above, 1−1.5 eV higher than those reported by other workers in studies

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concerned with CeO_2, Ce_2O_3, and La_2O_3 oxides, as well as systems containing mixtures thereof.[6,12,13,20,21] A similar discrepancy also occurs as far as the Ce3d (u‴) results are concerned.[6,12,13] What seems to be the main problem with these results is their comparatively large variability, though all of them were taken with the same instrumental apparatus. Indeed, while it is my contention that BE O1s = 529.0 ± 0.2 eV and BE Ce3d(u‴) = 916.6 ± 0.1 eV are the accurate results to be expected from the samples measured by Reddy et al.,[1,6,12,13,20,21] including the O1s results relevant to La_2O_3,[6] it should be also recalled that a certain variability was found for both transitions (especially the O1s) among the results taken by different groups. Henderson et al.[21] proposed that the quantity (let us call it H): H = BE Ce3d(u‴) − BE O1s, could be a more useful parameter to evaluate the chemistry of cerium oxidized systems on a comparative basis. Provided that the linearity of the BE scale is properly established and assessed,[14] this quantity is independent from the uncertainty associated with the choice of a reliable BE reference. However, even H "fluctuates" over a range of 0.7 eV for the samples listed in Table 2, the pure ceria sample featuring the lowest value (387.1 eV), while both samples $Ce_2O_3-La_2O_3$ 873 and $Ce_2O_3-La_2O_3$ 1073 feature the highest (387.8 eV). Moreover, H does not vary distinctly on passing from pure ceria to all the members of the CL series, as this variation is as low as +0.2 eV with sample $Ce_2O_3-La_2O_3$ 973, nor does it show any well-precise trend along the set of the CL series as a function of temperature. As a consequence, the (alleged) BE shift of 1 eV between the peak maxima of the O1s spectrum belonging to ceria and the four remaining samples, respectively, which Reddy et al. report in Figure 5 is mostly caused by a poorly accurate alignment of the spectra. In view of all this, I could share Reddy et al.'s statement that such a shift "gives an impression that the La^{3+} is combined with ceria to form a Ce−O−La type bond" only if the term "impression" means the peculiar hope that their O1s results have a real diagnostic value. In fact, these results, like all the BE results reported in their paper seem to be affected by (unknown) uncertainties arising from BE calibration problems with insulating surfaces. A very insightful and thorough study by El-Fallah et al.[22] showed that charging phenomena in XPS experiments of ceria surfaces can meaningfully affect the accuracy and reproducibility not only of the position and lineshape of the spectra but also of the [O]/[Ce] atomic ratio, a quantity which—oddly enough—Reddy et al. did not measure, though it would seem relevant and useful to the aims of their paper.

To conclude, if substitution of La_2O_3 sites for CeO_2 sites does indeed reflect on the oxidation state of cerium ions sitting on the surface of the CL solid solutions, such an inference cannot be substantiated from the experimental evidence shown in Figures 2 and 5 of the paper by Reddy et al. because this evidence is overwhelmingly affected by X-ray induced reduction phenomena and flawed with BE calibration uncertainties which make the verification of any hypothesis based on XPS Ce3d and O1s spectra a matter of mere speculation. Similarly, the spectra of Figure 3 say very little or nothing about the Ce^{3+}/Ce^{4+} "fluctuation" proposed by Reddy et al. because interference problems between Ce4d and La4d signals are so large that they preclude an accurate determination of the oxidation state of the cerium ion(s). Their work also confirms the many, subtle, challenging difficulties involved in the XPS spectra of CeO_2, which are still the subject of seminal research.[23]

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Received March 12, 2010. Revised Manuscript Received June 9, 2010

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