CHEMISTRY OF
MATERIALS
Comment

Chem. Mater. **2010,** *22,* 4517–4518 4517
DOI:10.1021/cm101719t

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

At the outset we wish to thank the author[1] for commenting on the XPS analysis of $CeO_2-La_2O_3$ (CL) solid solutions described in our publication.[2] As explicitly mentioned in the article, the XPS technique was used as a complementary tool to substantiate some of the observations made from other major techniques such as X-ray diffraction, Raman spectroscopy, transmission electron microscopy, UV–visible diffuse reflectance spectroscopy, and temperature programmed reduction. The XPS analysis was made purely based on literature reports with appropriate references. We should have referenced the relevant works of Prof. Paparazzo[1] in our paper. We regret this omission.

In the article[2] the complex multipeaked Ce 3d are labeled following the de facto standard nomenclature given by Burroughs et al.,[3] who were the first to interpret this spectra. The CL's Ce 3d core level spectra have revealed ~0.5 eV difference (see Table 2)[2] with reference to an earlier publication by Trovarelli.[4] Interestingly, similar binding energies were reported in many other publications in which C 1s (284.6 eV) has been used as a reference material for BE corrections.[5-15]

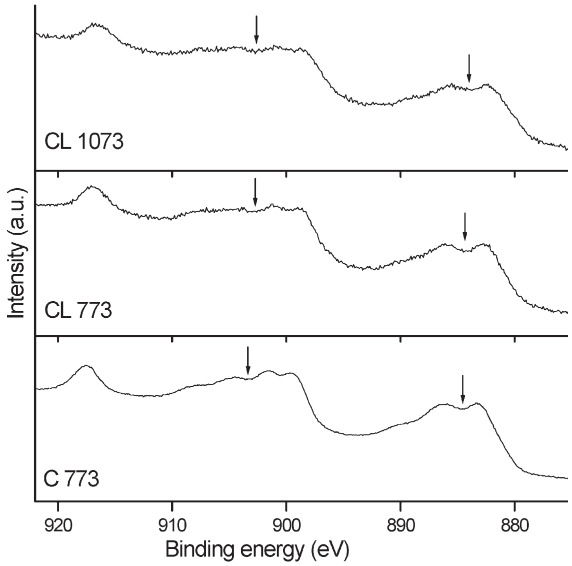

Figure 1. Ce 3d XPS core level spectra of ceria (C 773 K) and ceria-lanthana (CL 773 and 1073 K) samples.

It is well-known for those who are familiar with the application of XPS technique for chemical analysis what excitation energy sources are available, how the instrument is calibrated first using Cu $2p_{3/2}$, Cu $3p_{3/2}$, Ag $3d_{5/2}$, Au $4f_{7/2}$, and so forth, and how the binding energies are corrected with reference to adventitious carbon 1s, Ti $2p_{3/2}$, and so on. Therefore, making some unwanted comments on such established facts and typographic errors is just meaningless.

In our entire discussion[2] the undoped nanosized ceria is designated as pure ceria, and it does not mean that it exhibits only the pure Ce(IV) state. Simply misunderstanding the description of pure ceria, an entire series of comments were made which are unjustifiable. The pure ceria sample that we described was prepared under identical conditions of the $CeO_2-La_2O_3$ solid solutions. It is permissable to write nonstoichiometric ceria ($CeO_{2-\delta}$) as CeO_2, and it is also very well-known that CeO_2 should not be considered as Ce^{4+} alone with a configuration describable as $4f^0L^n$, but as a mixed $Ce^{4+}-Ce^{3+}$ state, that is, mixed with a $4f^1L^{n-1}$ configuration (L^n denotes O $2p^6$) due to the very similar energies of the 4f and orbital ligand valence levels.[4] Moreover, nanosized ceria itself is more defective and associated with a relatively larger amount of Ce^{3+} ions compared to the bulk ceria, and it is also inline with the relatively intense high binding energy component peak of the O 1s core level spectrum that is observed due to adsorption of surface residues.[2]

Ji et al.[16] reported that if CeO_2 contains only a small amount of Ce^{3+}, then the valleys are well-defined, but if the degree of reduction of Ce^{4+} to Ce^{3+} is high, then Ce^{3+} becomes more concentrated, and the valleys between v and v′ and u and u′ start to vanish. On the basis of those lines, we have tried to correlate the Ce^{3+} and Ce^{4+} ions with the valley depth (Figure 1). In the subsequent

---

(1) Paparazzo, E. Chem. Mater. **2010**, *22*, doi: 10.1021/cm100735n.
(2) Reddy, B. M.; Katta, L.; Thrimurthulu, G. *Chem. Mater.* **2010**, *22*, 467.
(3) Burroughs, P.; Hamnett, A.; Orchard, A. F.; Thornton, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1686.
(4) Trovarelli, A. In *Catalysis by Ceria and Related Materials, Catalytic Science Series*; Hutchings, G. J., Ed.; Imperial College Press: London, 2002; Vol. *2*.
(5) Damyanova, S.; Pawelec, B.; Arishtirova, K.; Huerta, M. V. M.; Fierro, J. L. G. *Appl. Catal., A* **2008**, *337*, 86.
(6) Arias, A. M.; García, M. F.; Hungría, A.-B.; Conesa, J. C.; Munuera, G. *J. Phys. Chem. B* **2003**, *107*, 2667.
(7) Gamarra, D.; Munuera, G.; Hungrí, A. B.; García, M. F.; Conesa, J. C.; Midgley, P. A.; Wang, X. Q.; Hanson, J. C.; Rodríguez, J. A.; Arias, A. M. *J. Phys. Chem. C* **2007**, *111*, 11026.
(8) Gayen, A.; Priolkar, K. R.; Sarode, P. R.; Jayaram, V.; Hegde, M. S.; Subbanna, G. N.; Emura, S. *Chem. Mater.* **2004**, *16*, 2317.
(9) Albero, J. S.; Reinoso, F. R.; Escribano, A. S. *J. Catal.* **2002**, *210*, 127.
(10) Damyanova, S.; Perez, C. A.; Schmal, M.; Bueno, J. M. C. *Appl. Catal., A* **2002**, *34*, 271.
(11) Haro, M. L.; Aboussaí, K.; Gonzalez, J. C.; Hernández, J. C.; Pintado, J. M.; Blanco, G.; Calvino, J. J.; Midgley, P. A.; Guillemaud, P. B.; Trasobares, S. *Chem. Mater.* **2009**, *21*, 1035.
(12) Chen, G.; Xu, C.; Song, X.; Xu, S.; Ding, Y.; Sun, S. *Cryst. Growth Des.* **2008**, *8*, 4449.
(13) Liu, G.; Rodriguez, J. A.; Hrbek, J.; Dvorak, J.; Peden, C. H. F. *J. Phys. Chem. B* **2001**, *105*, 7762.
(14) Colina, J. Z.; Nix, R. M.; Weiss, H. *J. Phys. Chem. B* **2005**, *109*, 10978.
(15) Colón, G.; Navío, J. A.; Monaci, R.; Ferino, I. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4453.
(16) Ji, P.; Zhang, J.; Chen, F.; Anpo, M. *J. Phys. Chem. C* **2008**, *112*, 17809.

sentence we have mentioned that "under high vacuum conditions during the XPS measurements there is a possibility of $Ce^{4+} \rightarrow Ce^{3+}$ reduction".[2] The X-ray dose is the same for all the samples. Besides the X-ray dose several other factors also such as secondary electrons from the X-ray source, sample charging, chemical environment, temperature, vacuum, and so forth influence the ceria reduction.[17] As a result of the chemical environment change (attributed to the formation of Ce–O–La) the CL 773 has shown comparatively high Ce^{3+} than the C 773 sample. Further, a reasonably larger amount of Ce^{3+} for CL 1073 K over CL 773 K may be due to UHV conditions where highly mobile surface oxide ions are extracted easily from the surface.[18] The evolution of O_2 under thermal treatments is responsible for the slight decrease of the u‴.[17,19]

Ce 3d is more surface sensitive than the Ce 4d; consequently, the latter results an unresolved and relatively noisey spectrum. The shape of the complex region, further, cannot be interpreted in detail unlike Ce 3d because of the 4d–4f interaction, which is much stronger than the 3d–4f coupling and introduces strong multiplet effects.[20] Therefore, we have presented the Ce 4d for secondary information only to support the Ce 3d results. The author is claiming that "there is an overlapping contribution from the La 4d to Ce 4d".[1] As per the literature reports, a highly intense doublet is observed at ~101 and ~105 eV, respectively, for La $4d_{5/2}$ and La $4d_{3/2}$.[21–26] There are no peaks observed in the middle of the trough of La 4d. Additionally, there is a peak observed at ~103.3 eV for Ce 4d attributed to Ce^{3+}; hence, we have assigned the same. In addition, it should be mentioned here that quantitatively we have not expressed the Ce^{3+}/Ce^{4+} ratio. We have outlined only the coexistence of both the oxidation states. Even if there is any contribution from La 4d, that is beyond our discussion.

B. M. Reddy,* L. Katta and G. Thrimurthulu
Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, 500 607, India

Received June 20, 2010

---

(17) Fallah, J. E.; Hilaire, L.; Roméo, M.; Normand, F. L. *J. Electron. Spectrosc. Relat. Phenom.* **1995**, *73*, 89.
(18) Koel, B. E.; Loubriel, G. M.; Knotek, M. L.; Stulen, R. H.; Rosenberg, R. A.; Parks, C. C. *Phys. Rev. B* **1982**, *25*, 5551.
(19) Laachir, A.; Perrichon, V.; Badri, A.; Lamotte, J.; Catherine, E.; Lavalley, C. J.; Fallah, J. E.; Hilaire, L.; Normand, F. l.; Quemere, E.; Sauvion, G. N.; Touret, O. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1601.
(20) Gamża1, M.; Ślebarskil, A.; Rosner, H. *Eur. Phys. J. B* **2008**, *63*, 1.
(21) Signorelli, A. J.; Hayes, R. G. *Phys. Rev. B* **1973**, *8*, 81.
(22) Briggs, D.; Seah, M. P. *Practical Surface Analysis by Auger and X-ray Photo Electron Spectroscopy*; Wiley: New York, 1983.
(23) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F. In *Handbook of X-ray Photoelectron Spectroscopy*; Mullenberg, G. F., Ed.; Perkin-Elmer Corporation: Eden Prairie, MN, 1978.
(24) Klyushnikov, O. I.; Sal'nikov, V. V.; Bogdanovich, N. M. *Inorg. Mater.* **2002**, *38*, 261.
(25) Ling, H.; Lu, X.; Li, A.; Wu, D.; Shao, Q.; Sheng, J.; Liu, Z.; Ming, N.; Wang, X.; Nguyen, B.-Y.; Zhou, H. *Appl. Phys. A: Mater. Sci. Process.* **2005**, *80*, 641.
(26) Broussard, P. R.; Qadri, S. B.; Cestone, V. C. *Appl. Surf. Sci.* **1997**, *115*, 80.