



Uppsala University
Structural Chemistry Department
Box 538, 751 21 Uppsala
jolla@kemi.uu.se

Final report
Project number: 17-537



Final report

Improving low temperature CO oxidation with nanostructured ceria

By: Jolla Kullgren

Contents

| | |
|-------------------|----|
| Abstract..... | 2 |
| Introduction..... | 3 |
| Methodology..... | 7 |
| Results..... | 7 |
| References..... | 16 |

Abstract

Incomplete CO oxidation during motor vehicle cold starts is a significant source of harmful CO emissions. With new, more fuel efficient engines there is a slow heating of the catalyst leading to a significant time delay in the onset of CO oxidation. This is now one of the major bottleneck in terms of improving reduction of emissions. Many alternatives have been explored in attempts to find good candidates for low temperature CO oxidation. However, these typically depend upon the use of expensive noble metals. At the same time nanostructured inexpensive Cerium dioxide (CeO_2 , ceria) have demonstrated promising results. The current proposal seek to unravel the mechanisms at play in this low temperature oxidation using theoretical simulations and aim to determine what type of surface structures that are beneficial/detrimental for this oxidation.

Ceria is well known for its oxygen chemistry and one very characteristic feature of ceria, and the main reason for its usefulness in for example CO oxidation, is its remarkable oxygen storage capacity (OSC); its ability to release and store oxygen under a wide range of atmospheric conditions. This ability originate from the special reduction-oxidation properties of Ce, namely the facile change in oxidation state between +4 and +3 that the cerium cations can undergo thanks to their reactive f -electrons. There is increasing recognition that peroxides (O_2^{2-}) and superoxides (O_2^-), collectively referred to as reactive oxygen species (ROS), play a significant role in many of the reactions taking place at the surfaces of reducible oxides. In the case of low temperature oxidation of CO using nanostructured ceria, superoxides were identified as the active species (Guzman et al., 2005). Such superoxides may form from the interaction, binding and charge transfer between O_2 molecules and the surface. For example, localised f -electrons at Ce^{3+} sites in the ceria surface may be transferred to an adsorbed O_2 :



In recent theoretical studies, we demonstrated that such transfer does not take place at the extended facets of the particles, but only at specific sites such as those at ridges and vertices, so-called “nanomotifs”. These findings are consistent with experimental findings of Wu *et al.* (Wu et al., 2010) demonstrating strong surface dependent preference for super- and per-oxide formation upon O₂ adsorption on nano-ceria. The aim of this project is to provide the rationale behind this dependence and to classify nanomotifs in terms of their ROS activity. This information will be very valuable for a rational design of new catalysts.

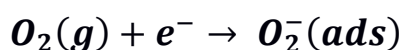
Introduction

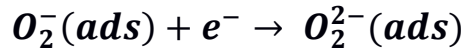
Metal oxides are one of the most important classes of solid material from both the fundamental and applied perspectives, and they play crucial roles in diverse technologies such as microelectronics, catalysis, fuel cells and gas sensors, to name a few. Much of the chemistry of metal oxides depends critically upon the structure of their surfaces, and in particular, upon the presence of defects, such as impurities and vacancies. Such defects typically possess special chemical and electronic properties compared to the regular portions of surface, which can be either beneficial or detrimental to the material’s functionality in a given application. Thus, a thorough knowledge and understanding of the structure of oxide surfaces is crucial to improving their functionality in existing technological applications and also to developing new ones.

The rich oxygen chemistry of reducible metal oxides rests heavily on the creation and annihilation of oxygen vacancies but it is now also well

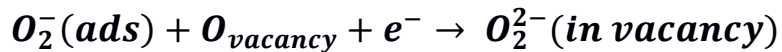
established that reactive oxygen species (ROS), such as the superoxide ion O_2^- , play key roles in redox processes occurring on *small* nanoparticles of reducible metal oxide; this has been demonstrated in many experiments.(Ahmad et al., 2014; Renuka et al., 2015; Tschope et al., 1995; Wang et al., 2008; Xu et al., 2010) In fact nanoparticle-based superoxide chemistry has been found relevant in diverse applications, where low temperature oxidation of CO as an alternative to expensive noble metals(Royer and Duprez, 2011) is what is relevant to the current project. Thus experiments(Ahmad et al., 2014; Bedilo et al., 2005; Renuka et al., 2015; Tschope et al., 1995; Wang et al., 2008; Xu et al., 2010) for *small* NPs of CeO_2 , ZrO_2 and Co_3O_4 have found that these demonstrate extraordinary redox activities compared to larger particles or extended surfaces, and show the presence of superoxide ions (O_2^-). Electron Paramagnetic Resonance (EPR) and Temperature Programmed Desorption (TPD) signals suggest that the superoxide ions are bound to the NPs as an integral part – but with structures that are virtually unknown. In will refer to these as *super-stoichiometric* NPs in the following, super referring to both superoxide and super- as in “extra-” or “over-“. Clearly both the stabilities of these NP– O_2^- species and their reactivities must be closely connected to their structures and shapes – but the relations are not known This is consistent with the current status of superoxide chemistry as a whole: the Chemical Reviews overview "*Superoxide ion: Generation and chemical implications*" from 2016(Hayyan et al., 2016) Hayyan *et al.* stated the proclaimed the need of elucidating the area of superoxide chemistry as it enters into so many disciplines

Reactive oxygen species (ROS) can form when available electrons at a surface react with an adsorbed O_2 molecule:





Superoxides ($\mathbf{O_2^-}$) and peroxides ($\mathbf{O_2^{2-}}$) have different characteristic and reactivity and exactly what species is formed is therefore of crucial importance to the reactivity of the surface and varies with situation. In metal oxides, the presence of ROS species will depend crucially on the availability of oxygen vacancies that can eliminate them according to the following reactions:



Regarding metal oxide nanoparticles, it was demonstrated already in 1995 by Tschöpe *et al.* that low temperature CO oxidation in $\mathbf{O_2}$ over small ceria nanoparticles proceeded without the involvement of oxygen vacancies, as often assumed to be the case, but rather through the interaction with superoxides present in these structures.(Tschöpe *et al.*, 1995) Wang *et al.*(Wang *et al.*, 2008) found a strong correlation between the amount of superoxide species in their $\mathbf{Co_3O_4}$ nanoparticles and sustained activity towards low temperature CO oxidation. The amount of superoxide species present in their particles, controlled by the calcination temperature, was also strongly connected with the morphology of the particles. Several routes leading to structures with appreciable amounts of superoxide species was also presented for nanoparticles of $\mathbf{ZrO_2}$ (Bedilo *et al.*, 2005) which is a far less reducible metal oxide. This naturally raises a question that I aim to answer within the scope of the current project, namely: *“How important is it that the metal ions is reducible, might the needed electrons (to form superoxide ions) come from stoichiometry and the shape of particle itself?”*

The picture emerging from the experimental studies above is that, when small, metal oxide nanoparticles are prone to form super-stoichiometric structures (distinct and active structures with a surplus of oxygen and with

superoxide ions as an integral part) with sustained activity towards e.g. CO oxidation.

In general, theory from extended surface studies predicts that superoxide ions are only metastable species that readily undergo a transformation to less reactive peroxides or monatomic $O^{\delta-}$ species.(Conesa, 2009; Setvín et al., 2013; Xia et al., 2012; Zhao et al., 2012) Simulations on nanoparticle models have mainly focused on describing the redox activity in terms of oxygen vacancies(Loschen et al., 2008; Migani et al., 2010; Preda et al., 2011; Ruiz Puigdollers et al., 2016) Superoxide ions was considered in some of these studies, but again predicted them to be unstable. Clearly, there is a need for alternative models to explain the sustained (superoxide) activity seen for very small nanoparticles of CeO_2 , Co_3O_4 and ZrO_2 . In recent theoretical publications on CeO_2 (Huang and Beck, 2015; Kullgren et al., 2013), one alternative model to explain the phenomena was put forward. The crucial perspective in these studies is the inclusion of the superoxide species as an integral part of the structures (intrinsic superoxide ions using the notion of Huang & Beck(Huang and Beck, 2015)). When particles are small (below 5 nm) the ground-state is an one with appreciable amount of such intrinsic superoxide ions present, the morphology is also different from the one predicated using stoichiometric models. The perspective adopted in these theoretical simulations have been supported in subsequent measurements(Renuka et al., 2015). **Fig. 1** illustrates the new perspective in relation to the prevailing one. In the current project this model have been scrutinized and possible alternatives have been explored.

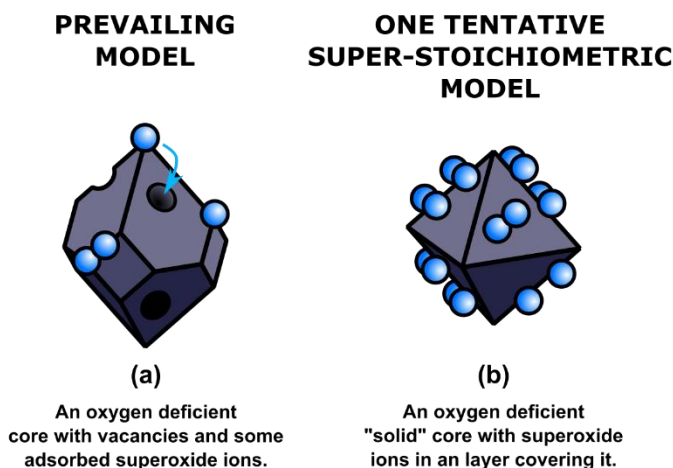


Figure 1. Two mechanisms used to explain efficient oxygen chemistry of metal oxide nanoparticles. **To the left:** oxygen vacancies are the key species. Formation of vacancies in a stoichiometric structure is associated with formation of reduced cations. These reduced cations can transfer electrons to adsorbing oxygen molecules thereby creating superoxide ions. These, however, will be subsequently eliminated by the vacancies leading to deactivation of the nanoparticle. The latter process is in conflict with experimental observation. **To the right:** A stable structure with intrinsic superoxide ions is the central species, its morphology is different from the stoichiometric particle.

Methodology

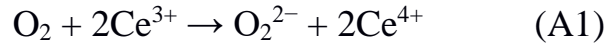
The theoretical simulation presented here are based on density functional theory (DFT) in the implementation with plane waves and pseudopotentials. More specifically, we used the generalized gradient corrections to the local density functional approximations as proposed by Perdew *et al.* (PBE). The software package VASP have been used throughout.

Results

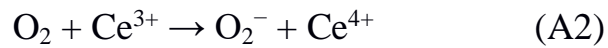
One central theme in this project is to find descriptors that help us predict and understand where and when different reactive oxygen species (ROS) forms at the ceria surface. In parallel and together with this work I am also focusing on pinpointing the role of the cation reducibility in the ROS formation process. These efforts are described in sub-section C below.

A. The role of local electrostatic potential in the formation of ROS species

As mentioned, superoxides and peroxides, can be formed through a reaction between an O₂ molecule and a surface with available electrons. In the case of the ceria surface, such reactions can be written as:

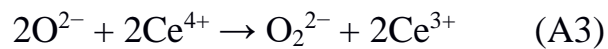


for peroxides, and as:

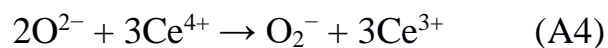


for superoxides.

The energetics of these reactions have been studied theoretically when occurring on extended surfaces (Huang and Fabris, 2007; Kullgren et al., 2014) and on nanoparticles (Huang and Beck, 2015; Kullgren et al., 2013; Preda et al., 2011). Peroxides and superoxides can also, in principle, be formed natively by a direct reaction between lattice oxygen ions according to:



for peroxides, and as:



for superoxides. I will refer to these latter species as native ROS species.

In the native formation of ROS in the bulk, and on the extended (111) and (110) surfaces, the theoretical simulations consistently predict that peroxides are more stable than superoxides. However, these native species are unstable w.r.t the stoichiometric crystal. Peroxy formation energies, E_f , follow the order of stability $E_f^{(110)} < E_f^{(111)} < E_f^{\text{bulk}}$. Interestingly, at the (110) surface, the formation of these native peroxides can be stabilized if accompanied by superoxide formation through reaction A2(Kullgren et al., 2014). One aim in the current project has been to determine the role of such coupled reactions in the context of ceria nanostructures and to find some general principles linking the local atomic structure and electrostatic potential with the stability and type of ROS species (super- or per-oxides) formed at various structural motifs at the ceria surface. **Fig. 2** show the three low index surfaces of CeO₂. The figure also indicate their connection to common nanostructures that can be synthesized experimentally, namely octahedral particles (the equilibrium shape), nanocubes and nanowires. The color map to the far right in the figure show a map of the electrostatic potential for the surfaces with all values given with respect to the vacuum level.

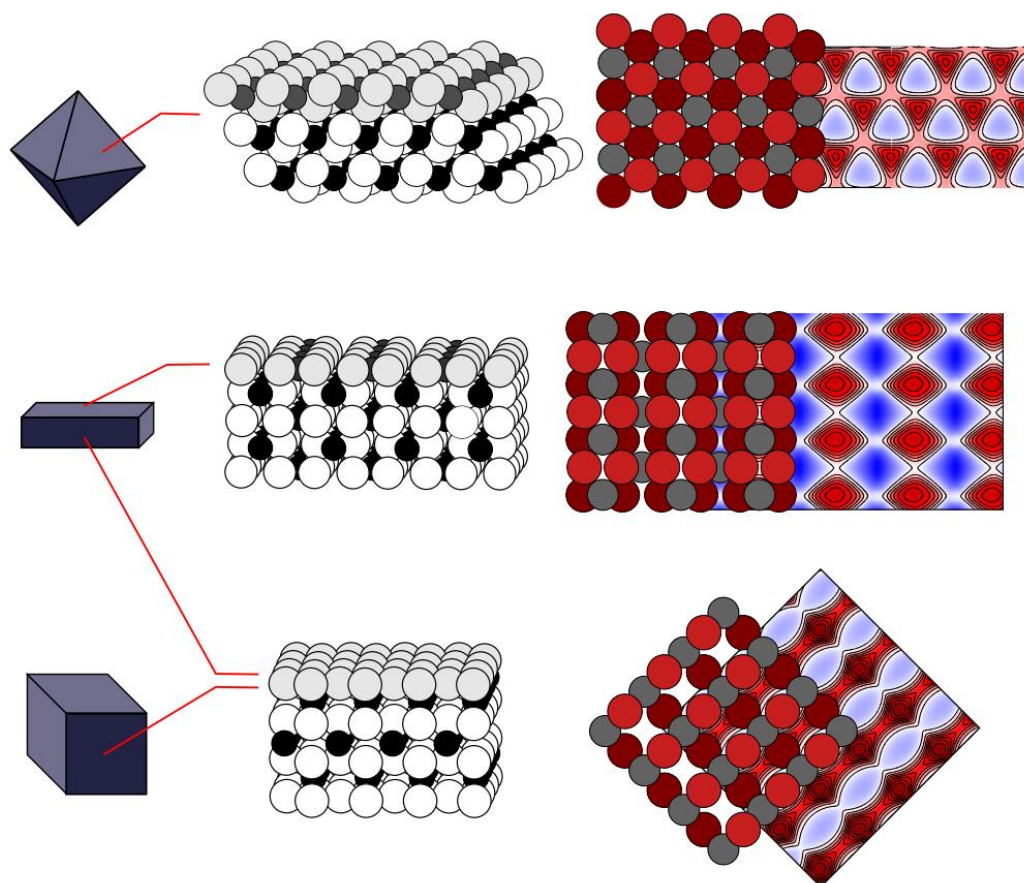


Figure 2. Relation between nanoparticle shape and surface exposed. Top panel: octahedral particles and the (111) surface. Middle panel: nanowires and the (110) surface. Bottom panel: nanocube and the (100) surface. Color map to the right show the variation in electrostatic potential across the various surfaces projected on. The maps were constructed by projecting the electrostatic potential, calculated with respect to the value in the middle of the vacuum gap in each case, onto isosurfaces of constant charge density corresponding to $0.01 \text{ e}/\text{\AA}^3$

Each of the low-index surfaces form different ROS species upon O_2 adsorption, (111): O_2 , (110): O_2^- and (100): O_2^{2-} . Based on my DFT data, there seems to be a correlation between the type of ROS species formed and the local coordination around the O_2 entity that can be summarized in the following way:

- O_2 species strongly coordinated to one cerium ion are most stable as superoxide species (sites on the (110) terrace)
- O_2 species strongly coordinated to more than one cerium ion are found as peroxide species (vacancy sites and 100 surfaces)

- physisorption occurs when strong coordination cannot be achieved (sites at the (111) terrace)

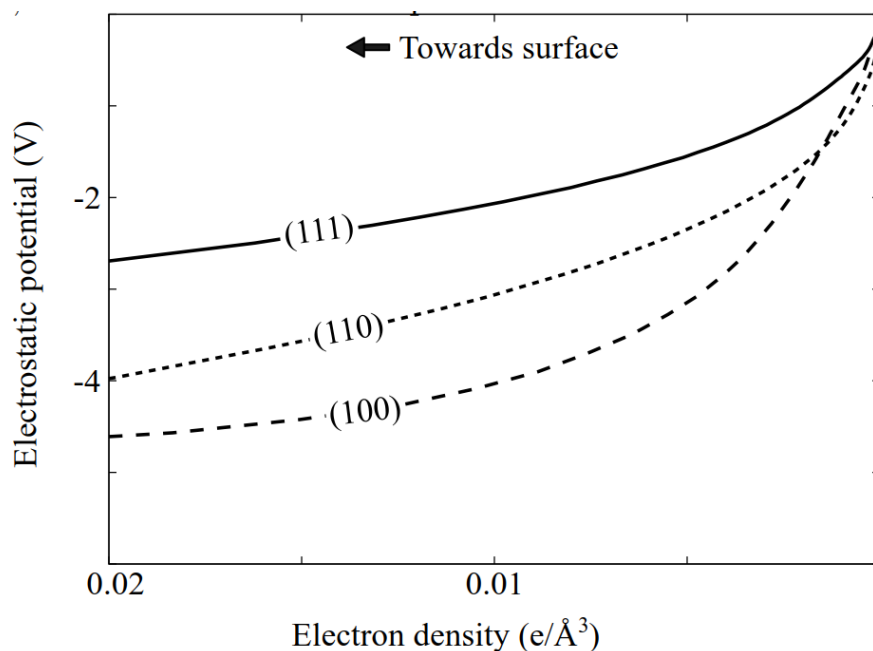


Figure 3. Electrostatic potential as a function of electron density on approaching the surfaces along the z-direction towards the respective minimum on the electrostatic potential maps in Fig. 2.

In order to see whether we can relate the type of ROS formed with the local electrostatic potential at the surface, I compare the electrostatic potential to what species that forms. **Fig. 3** show the variation in electrostatic potential as a function of electron density on approaching the surfaces along the z-direction towards the respective minimum on these electrostatic potential maps (the darkest red in **Fig. 2**). There is pleasing trend among these curves where the deepest electrostatic potential favors the formation of the more negatively charged species.

B. Coverage dependence on the O₂ adsorption energy

We have identifies a strong coverage dependence in the O₂ adsorption energy. In general, with less oxygen's being adsorbed, or with more Ce³⁺ being present, the oxygen binds stronger. Here, we used the Ce₄₄O₈₀ and

$\text{Ce}_{19}\text{O}_{32}$ nanoparticle models calculated individual oxygen adsorption energies by adding O_2 molecules one by one, optimizing the whole structure each time. There are 16 and 12 Ce^{3+} in the $\text{Ce}_{44}\text{O}_{80}$ and $\text{Ce}_{19}\text{O}_{32}$ cluster respectively. Both $\text{Ce}_{44}\text{O}_{80}$ and $\text{Ce}_{19}\text{O}_{32}$ clusters give similar results and I only show the data for the $\text{Ce}_{44}\text{O}_{80}$ in the following.

From this data it becomes clear that, the oxygen adsorption energy for ridges and corners of a nanoparticle are very different, in line with the difference in coordination number of the Ce ion to which the O_2 is adsorbed. The binding energies at corners are stronger than on the ridges, by more than 0.5 eV. Within the two populations (corners and ridges), the oxygen adsorption energy decreases/increases linearly with the number of the $\text{O}_2/\text{Ce}^{3+}$ in the cluster but with different slopes.

The slope is larger for the corners. This strong dependence has a significant influence on the width of the simulated Temperature Programmed Desorption (TPD) spectra (using micro kinetic modelling). The broad TPD spectra is in agreement with experiment findings.

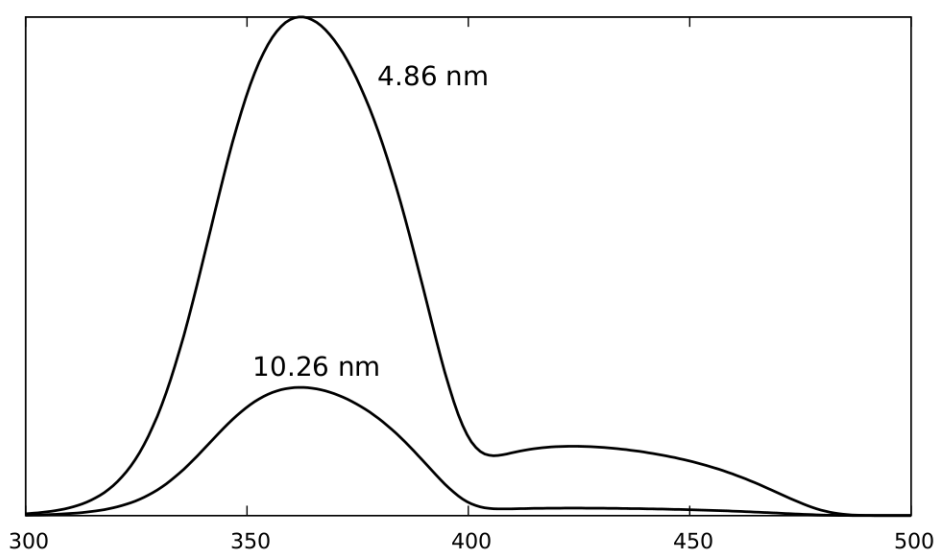


Figure 4. Simulated TPD spectra using DFT-based micro kinetic modelling.

The strong dependence of O₂ desorption energy on the amount of Ce³⁺ opens up for the possibility to tune the oxygen reactivity by controlling the amount of adsorbed O₂ or amount of Ce³⁺ in the cluster. We have a manuscript under review in the journal of catalysis discussing these matters in more detail.

C. The role of reducibility in the ROS formation and reactivity

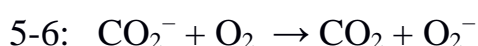
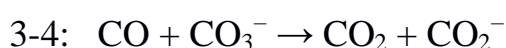
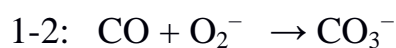
In a recent publication, we have shown that small ceria nanoparticles are most stable when they are in a super-stoichiometric state (see **Fig. 1**). With super-stoichiometric state, we refer to a particle with superoxide species as an integral part of without the presence of any reduced cations. Whether the reactivity of such particle is mainly dictated by the superoxide species themselves or if the reducibility of the cation is of fundamental importance is not clear. We may also ask whether super stoichiometric structures requires a reducible cation (despite them not being present in the final structure). To address these questions I consider CeO₂, ZrO₂ and HfO₂. They can all be found in the cubic fluorite structure allowing for a systematic comparison. While this is the most stable phase for CeO₂ under a wide range of conditions both ZrO₂ and HfO₂ tend to preferentially crystallize into a monoclinic structure. However, in the case of small nanoparticles they often adopt either the cubic structure or a third, a tetragonal one. The critical diameter for the cubic/tetragonal to monoclinic transition has been estimated, experimentally, to be about 20 and 5.5 nm for ZrO₂ and HfO₂, respectively (Forker et al., 2008).

In my comparison of the various metal oxides, I consider the under-, over- and perfectly-stoichiometric models devised in Ref. (Kullgren et al., 2013). Using DFT simulations, I can show that, for all systems and particle sizes up to 3 nm, the supercharged particles are the most stable ones. As expected, the under-stoichiometric (reduced) particles are more unstable in

the case of ZrO_2 and HfO_2 . At the same time, the super-stoichiometric particles are much more stable than the corresponding perfectly stoichiometric ones in the case of ZrO_2 and HfO_2 compared to CeO_2 .

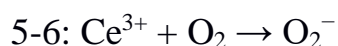
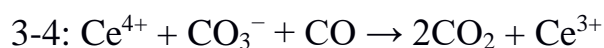
One may now ask “Is the superoxide chemistry the same?” To address this question I used the smallest super-stoichiometric models (Me_6O_{21}) and considered tentative intermediate species in the CO oxidation reaction.

CO oxidation using superoxide species may proceed through the following (hypothetical) reaction steps:



The numbers in front of the reaction are labels used in the energy diagram presented in **Fig. 5**.

In comparing the two systems I find that, while the ZrO_2 is able to stabilize all intermediates above with an essentially monotonically decreasing trend in energies, the CeO_2 cluster is not capable of stabilizing the CO_2^- species. In this latter case, the reaction therefore proceed as follows:



The key difference here is that the CeO_2 cluster is not reliant on having the CO and O_2 approaching simultaneously to make the full conversion to CO_2 . Thus in a sense the Ce cluster has twice the capacity in oxidizing CO provided no extra oxygen is provided. This difference in behavior may also

reflect upon the kinetics which will be further addressed through calculation of reaction barriers. Thus, in conclusion the CO oxidation simulations suggests that both small particles of CeO_2 and ZrO_2 are capable of fully oxidizing CO in stoichiometric gas mixtures but the reaction proceeds according to different routes.

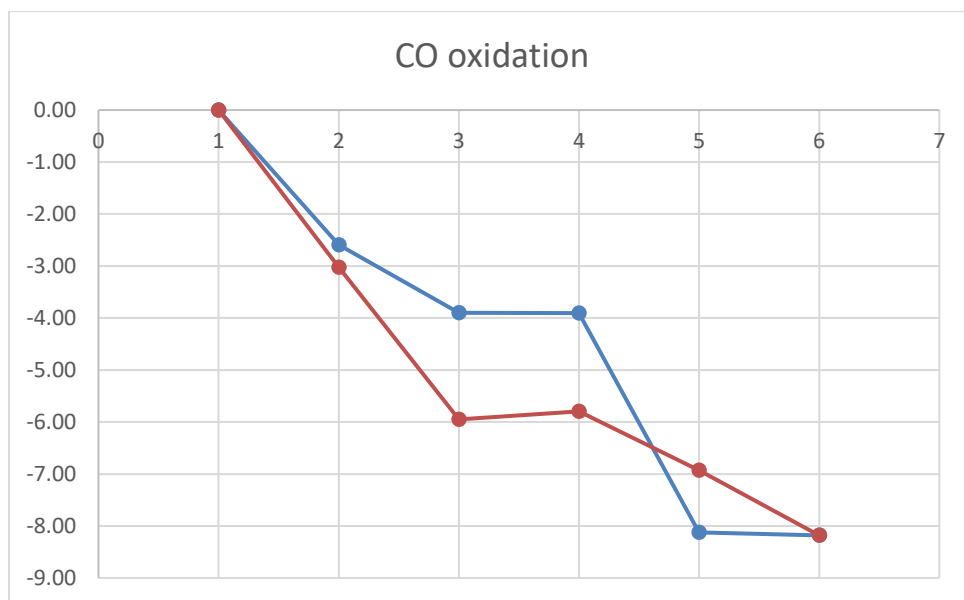


Figure 5. Energy diagram for CO oxidation using a Ce_6O_{21} and Zr_6O_{21} super-stoichiometric clusters. The x-axis indicate the various intermediate structures presented in reactions above. The y-axis gives energy in electron volts.

Outlook

My simulations suggests that non-reducible super-stoichiometric nanoparticles could be useful complements to the reducible dittos since they have a stronger stabilization of some reactive oxygen species that we know are important in oxidation catalysis. This suggest that there may be a prospect of using also non-reducible metal oxide in efficient low temperature CO oxidation.

References:

- Ahmad, S., Gopalaiah, K., Chandrudu, S.N., Nagarajan, R., 2014. Anion (Fluoride)-Doped Ceria Nanocrystals: Synthesis, Characterization, and Its Catalytic Application to Oxidative Coupling of Benzylamines. *Inorg. Chem.* 53, 2030–2039. <https://doi.org/10.1021/ic403166q>
- Bedilo, A.F., Plotnikov, M.A., Mezentseva, N.V., Volodin, A.M., Zhidomirov, G.M., Rybkin, I.M., Klabunde, K.J., 2005. Superoxide radical anions on the surface of zirconia and sulfated zirconia: formation mechanisms, properties and structure. *Phys. Chem. Chem. Phys.* 7, 3059–3069. <https://doi.org/10.1039/B504262C>
- Conesa, J.C., 2009. Surface anion vacancies on ceria: Quantum modelling of mutual interactions and oxygen adsorption. *Catalysis Today* 143, 315–325. <https://doi.org/10.1016/j.cattod.2008.11.005>
- Forker, M., de la Presa, P., Hoffbauer, W., Schlabach, S., Bruns, M., Szabó, D.V., 2008. Structure, phase transformations, and defects of HfO_2 and ZrO_2 nanoparticles studied by ^{181}Ta and ^{111}Cd perturbed angular correlations, ^1H magic-angle spinning NMR, XPS, and x-ray and electron diffraction. *Phys. Rev. B* 77, 054108. <https://doi.org/10.1103/PhysRevB.77.054108>
- Guzman, J., Carrettin, S., Fierro-Gonzalez, J.C., Hao, Y., Gates, B.C., Corma, A., 2005. . *Angew. Chem. Int. Ed.* 44, 4778.
- Hayyan, M., Hashim, M.A., AlNashef, I.M., 2016. Superoxide Ion: Generation and Chemical Implications. *Chem. Rev.* 116, 3029–3085. <https://doi.org/10.1021/acs.chemrev.5b00407>
- Huang, M., Fabris, S., 2007. . *Phys. Rev. B* 75, 081404.
- Huang, X., Beck, M.J., 2015. Size-Dependent Appearance of Intrinsic O_x “Activated Oxygen” Molecules on Ceria Nanoparticles. *Chem. Mater.* 27, 5840–5844. <https://doi.org/10.1021/acs.chemmater.5b02426>
- Kullgren, J., Hermansson, K., Broqvist, P., 2014. Reactive oxygen species in stoichiometric ceria: Bulk and low-index surfaces. *Phys. Status Solidi RRL* n/a-n/a. <https://doi.org/10.1002/pssr.201409099>
- Kullgren, J., Hermansson, K., Broqvist, P., 2013. Supercharged Low-Temperature Oxygen Storage Capacity of Ceria at the Nanoscale. *J. Phys. Chem. Lett.* 4, 604–608. <https://doi.org/10.1021/jz3020524>
- Loschen, C., Migani, A., Bromley, S.T., Illas, F., Neyman, K.M., 2008. Density functional studies of model cerium oxide nanoparticles. *Phys. Chem. Chem. Phys.* 10, 5730–5738. <https://doi.org/10.1039/B805904G>
- Migani, A., Vayssilov, G.N., Bromley, S.T., Illas, F., Neyman, K.M., 2010. Greatly facilitated oxygen vacancy formation in ceria nanocrystallites. *Chem. Commun.* 46, 5936–5938. <https://doi.org/10.1039/C0CC01091J>
- Preda, G., Migani, A., Neyman, K.M., Bromley, S.T., Illas, F., Pacchioni, G., 2011. Formation of Superoxide Anions on Ceria Nanoparticles by Interaction of Molecular Oxygen with Ce³⁺ Sites. *J. Phys. Chem. C* 115, 5817–5822. <https://doi.org/10.1021/jp111147y>
- Renuka, N.K., Harsha, N., Divya, T., 2015. Supercharged ceria quantum dots with exceptionally high oxygen buffer action. *RSC Adv.* 5, 38837–38841. <https://doi.org/10.1039/C5RA01161B>
- Royer, S., Duprez, D., 2011. Catalytic Oxidation of Carbon Monoxide over Transition Metal Oxides. *ChemCatChem* 3, 24–65. <https://doi.org/10.1002/cctc.201000378>
- Ruiz Puigdollers, A., Illas, F., Pacchioni, G., 2016. Effect of Nanostructuring on the Reactivity of Zirconia: A DFT+U Study of Au Atom Adsorption. *J. Phys. Chem. C* 120, 17604–17612. <https://doi.org/10.1021/acs.jpcc.6b05685>
- Setvín, M., Aschauer, U., Scheiber, P., Li, Y.-F., Hou, W., Schmid, M., Selloni, A., Diebold, U., 2013. Reaction of O₂ with Subsurface Oxygen Vacancies on TiO₂ Anatase (101). *Science* 341, 988–991. <https://doi.org/10.1126/science.1239879>
- Shahed, S.M.F., Sainoo, Y., Komeda, T., 2011. Scanning Tunneling Microscope Study of Surface Morphology Variation of CeO₂(111) with Changing Annealing Condition. *Jpn. J. Appl. Phys.* 50, 08LB05. <https://doi.org/10.1143/JJAP.50.08LB05>

- Tschope, A., Liu, W., Flytzanistephanopoulos, M., Ying, J.Y., 1995. Redox Activity of Nonstoichiometric Cerium Oxide-Based Nanocrystalline Catalysts. *Journal of Catalysis* 157, 42–50. <https://doi.org/10.1006/jcat.1995.1266>
- Wang, Y.-Z., Zhao, Y.-X., Gao, C.-G., Liu, D.-S., 2008. Origin of the High Activity and Stability of Co_3O_4 in Low-temperature CO Oxidation. *Catal Lett* 125, 134–138. <https://doi.org/10.1007/s10562-008-9531-4>
- Wu, Z., Li, M., Howe, J., Meyer, H.M., Overbury, S.H., 2010. Probing Defect Sites on CeO_2 Nanocrystals with Well-Defined Surface Planes by Raman Spectroscopy and O_2 Adsorption†. *Langmuir* 26, 16595–16606. <https://doi.org/10.1021/la101723w>
- Xia, X., J. Oldman, R., A. Catlow, C.R., 2012. Oxygen adsorption and dissociation on yttria stabilized zirconia surfaces. *Journal of Materials Chemistry* 22, 8594–8612. <https://doi.org/10.1039/C2JM16604F>
- Xu, J., Harmer, J., Li, G., Chapman, T., Collier, P., Longworth, S., Tsang, S.C., 2010. Size dependent oxygen buffering capacity of ceria nanocrystals. *Chem. Commun.* 46, 1887–1889. <https://doi.org/10.1039/B923780A>
- Zhao, Yun, Teng, B.-T., Wen, X.-D., Zhao, Yue, Chen, Q.-P., Zhao, L.-H., Luo, M.-F., 2012. Superoxide and Peroxide Species on $\text{CeO}_2(111)$, and Their Oxidation Roles. *The Journal of Physical Chemistry C* 116, 15986–15991. <https://doi.org/10.1021/jp3016326>