X-ray photoelectron spectroscopy of cerium and its oxides – 3d states

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**Abstract:** Cerium oxides are frequently used in the automotive industry as an active substrate in catalysts. In my doctoral study I prepare model systems of cerium oxides deposited on a rhodium monocrystal (so called inverse catalyst). The degree of oxidation of the cerium oxide changes with exposition of the surface with gases. In X-ray photoelectron spectroscopy (XPS) we can best study these changes on the 3d level.

In my recent work I challenged problem of fitting different 3d level spectra. This problem seems especially complex. The theory based on ab-initio calculations is built since 1973. To explain some charge transfers, DFT+U is used nowadays.

In my essay, I would like to question different contributions and peaks in the Ce 3d level spectra. I’ll try to explain my fitting process including its assumptions and estimate possible problems.

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The method of X-ray photoelectron spectroscopy (XPS) is a powerful method, which is capable to determine the chemical composition of a measured substrate. Moreover, this method is chemical sensitive, so it is possible to distinguish two different chemical states of a substrate component.

In the case of cerium, it’s very important to distinguish metal cerium, cerium oxide with cerium charge 3+ and cerium oxide with cerium charge 4+. Cerium oxide is actually used as the substrate oxide in catalysts where it serves as an oxide capacitor. Cerium oxide is, in fact, able to change its oxidation state from Ce$^{3+}$ to Ce$^{4+}$ in oxygen-rich conditions and from Ce$^{4+}$ to Ce$^{3+}$ in reducing conditions. During this process, oxygen is released and reacts with other reactants or is incorporated respectively, so the cerium oxide acts as oxide capacitor.
With the XPS method, we can best measure the 3d level of ceria, because of its binding energy ca. 900eV. While the metal cerium spectrum is quite simple to understand, because it has two peaks originating from spin-orbit splitting, the cerium oxide spectra are far more complex. The origin of the additional doublets comes from different screening effects during electron emission that was explained by Kotani and Toyozawa in 1973. The calculations were made by two different methods. One was the Green’s function method and the other was based on the exact solution of the one-electron states for a system with finite volume.

In the case of Ce$^{3+}$, we measure the spectrum composed of 2 doublets that correspond to two final state configurations - 3d$^9$4f$^1$(5d6s)$^d$ and 3d$^9$4f$^2$(5d6s)$^3$, while in the case of Ce$^{4+}$, we measure even 3 doublets corresponding to 3d$^9$4f$^0$(5d6s)$^5$, 3d$^9$4f$^1$(5d6s)$^4$ and 3d$^9$4f$^2$(5d6s)$^3$ final states. Due to different chemical surrounding, the peaks of final states from Ce$^{3+}$ and Ce$^{4+}$ are slightly shifted. So in the case of transitional state between Ce$^{3+}$ and Ce$^{4+}$, there could be 5 doublets on different energies. Moreover, the measurements by monochromatic high-resolution XPS method showed that unlike the others, one of the peak shape belonging to “4f$^2$” state is asymmetric and therefore it could be best fitted by summing two symmetric Voight-type peaks. But in my spectra measured on systems of so-called inverse catalyst (cerium oxide is deposited in discontinuous layers on rhodium (111) monocrystal), additional peaks were observed. I explain these peaks as Ce-Rh alloy states in my diploma work because they have binding energy similar to Ce-metal peaks.

According to new DFT+U calculations, additional effect of charge transfer can occur on discontinuous ceria layers. This effect cause that Ce$^{4+}$ appears on the spectra as Ce$^{3+}$, so the maximal oxidation of the layer is limited.

In the issue of chemical reactions, knowledge of chemical state of cerium oxide layer is required. By measuring the 3d level of ceria, we can determine the degree of oxidation of the cerium layer. By exposing the substrate, oxidation level changes in dependence on type of the exposing gas, surface temperature, surface morphology, degree of oxidation of the cerium layer and many other parameters.

So the papers from Kotani and Toyozawa helped the comprehension of number and position of the cerium oxide peaks. Other theoretical works solved even the question of the shape of the 3d level peaks. But experimentally known fact is that in the case of thin cerium oxide
layers, peak shapes and peak positions slightly differ in dependence on the substrate material. These effects aren’t still theoretically explained.

In last years, some DFT+U calculations were performed on model systems of cerium oxide deposited on Cu (111). These calculations were based on the supercell modelling method and the results were compared with atomic resolution STM measurements. But the calculations for the method of XPS are more complicated. Our model systems are grown on single crystals (Rh (111)), but the topmost (ceria) layer is discontinuous (with steps, islands, multiple layers, substrate material, different crystal faces, defects, …) and the degree of oxidation of particular islands differs in dependence on the island size. The measurements of these surfaces are not local, so the effects of averaging must be take account. In conclusion, the spectra are created by mixing up many different cerium oxide states, so the calculations for these systems are too complicated and the results of the theoretical calculations do not have to agree with measured spectra although they are correctly computed.

Another part is the reactivity measurement. Methods of thermal desorption spectroscopy (TDS) and molecular beam (MB) are used to measure the surface reactions. In my work, we concentrate on oxidation of carbon monoxide as an important part of three way catalysis (TWC). These methods are also non-local, so we measure the products from the whole surface. Moreover, these processes are dynamic – gas molecules bombard the surface, adsorb on the surface, diffuse, react and desorb back to vacuum and the only thing we measure is the flow of the back-scattered molecules in the dependence on temperature or time. So all our results are strongly dependent on sample quality, precision during preparation and also on parameters we change systematically. In theoretical approach, we can count every react position and every reaction path, but the results will be only a mixture of all these processes, which is expressed by single parameter like activation energy of desorption.

Easier to system characterization is to measure step-by-step – first measure the clean single crystal substrate with XPS method, then adsorb some molecules (MB measurement) and measure the XPS spectrum again to see the electron-state changes. This way we can distinguish for example two different CO adsorption states – on-top and hollow with different binding energy. This way the theoretic calculations helped to define the exact binding positions (infrared measurements, dynamic LEED measurements). Also then, the most favorable dissociation path can be counted. Similar computations can be made for both
reactants and we are capable to count the surface mobility. Then, by adding reaction and desorption parameters and reactions on the steps, we can adjust our model to experimentally measured signal.

Even after vacuum evaporation of ceria and its epitaxial growth in cerium oxide overlayer, favored adsorption sites and other parameters could be count. But with every step away from ideal single crystal surface, the system is harder to characterize. For example, in the case of cerium oxide, there are papers that describe the incorporation of the oxygen atoms into the rhodium single crystal. So with the increasing oxygen pressure, the cerium oxide islands could be oxidized:

1) directly by adsorbing oxygen molecules
2) by oxygen atoms that dissociated on substrate single crystal Rh (111) and diffused to Rh-Ce interface
3) by subsurface oxygen that diffuses in the single crystal

In the consequence, to describe precisely such a complex system and to obtain publishable results are two too complex tasks with too uncertain outcome.

When we concentrate on another part of the complicate process of determination of the cerium oxide state from Ce 3d level spectra, we must count also with effects like crystal system change. Cerium oxides can crystallize in several different crystal systems – while CeO$_2$ crystals in cubic crystal system, Ce$_2$O$_3$ crystals in hexagonal crystal system. These two compounds differ significantly in characteristics. So the catalytically active is the cubic form, which during the oxygen shortage stays in the cubic crystal system creating oxygen vacancies. But when this oxide recrystallizes, the hexagonal form is more stable and moreover, this form is not capable of oxidation to CeO$_2$. This recrystallization is thermally induced, so my model systems are stable only in some temperature range. In my work, I would like to investigate the process of this thermally induced relaxation. But in the theoretical approach, we have additional difficulty to face, because not only we must consider the Rh-Ce$_2$O$_3$ (cubic) interface, but also the Rh-Ce$_2$O$_3$ (hexagonal) interface can occur. And I haven’t mentioned yet the case with metallic cerium.

On the opposite, the main thing we want to determine is the degree of oxidation. So in the Ce 3d level spectra we fit the 5 doublets and determine the area of Ce$^{3+}$ and Ce$^{4+}$ peaks. From this analysis, we can measure the changes in the degree of oxidation. On the contrary, the
situation doesn’t have to be as easy understanding as it looks like. First thing is that the recrystallization occurs after heating my sample in oxygen atmosphere of $5 \times 10^{-7}$ Torr. But also the cerium peak heights and area lowers after this heating procedure. So there are some possible explanations, which would need the sharp eye of a theoretician:

1) Because of coalescence, the area of cerium oxide lowers, so the signal is lower.
2) The electron gain is lower (the sensitivity factor changes).
3) Cerium oxide was incorporated into rhodium single crystal, so fewer Ce 3d electrons are penetrating to the vacuum.

It is most probable, that lowering of the signal is due to all three reasons. The important thing is, which process is the most favorable.

Another complexity is the presence of metallic cerium. There are also several explanations, why this peaks appear in my spectra:

1) High reduction of discontinuous ceria layers
2) Low temperature Ce-Rh alloy formation
3) Another state with binding energy similar to metal cerium

In my opinion, the first two cases are most probable, because this peak occurs only after heating to $500^\circ C$ and only after high reduction. The formation of Ce-Rh alloy was already reported, but the heating temperatures were little higher. The sample was after the heating oriented with 2x2 LEED pattern. But some referees write, that formation of the Ce-Rh alloy is not likely, so any theoretical work aimed on these problems would be convenient.

In conclusion, complete theoretical description of my system of inverse catalyst CeO$_x$/Rh(111) is not yet possible. But theory can describe some more similar systems like thin layer epitaxial CeO$_2$ on Cu (111) or single crystalline Rh (111) and adsorption positions and reaction paths on its surface. Some other more similar issues could be solved by theoretic calculations to help me with explanations of my spectra: Oxidation of ceria islands (probability analysis, diffusion rates); Area of cerium oxide lowers after heating in oxygen atmosphere (DFT+U approach); Metallic cerium presence (ab-initio calculations). So the theory could help me in particular problems I face in my Ce 3d level analysis and is capable to push the frontiers of knowledge, but complete description of systems that are shifted to practical application is yet beyond its reach.
Used articles:


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