

Complexity of CO oxidation mechanisms on ceria-based catalysts uncovered by time-resolved X-ray absorption spectroscopy.

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Background

Spectroscopic identification of active sites and reaction intermediates in heterogeneous catalysts is typically very challenging. This is due to the low concentration of the active species and a large structural heterogeneity on the reactive surface.

Methods

At the SuperXAS beamline at the Swiss Light Source, we developed highly sensitive time-resolved fluorescence-detected X-ray spectroscopic methods and showed their high potential for the identification of the active species in ceria-based catalysts.¹ Previously, we used these methods under transient conditions to demonstrate that during CO oxidation on a Pt/CeO₂ catalyst the active Ce³⁺ species is short-lived and therefore can be observed only under transient conditions.² The results also quantitatively proved that the whole reaction proceeds via a Mars van Krevelen mechanism involving lattice oxygen and ceria reduction is kinetically coupled to the rate determining step of CO oxidation. At the same time, we identified the long-lived inactive spectator Ce³⁺ species which were stable under steady state conditions of CO oxidation.

Results

In this work we used similar experimental approach to address new questions about the CO oxidation mechanism on ceria-based catalysts. The main results are the following:

1. Active and spectator Ce³⁺ species exist simultaneously in Pt/CeO₂, Pt/Ce_{0.5}Zr_{0.5}O₂, Pt/Ce_{0.5}Sn_{0.5}O₂, and CuO-CeO₂ catalysts during low-temperature CO oxidation. They can be distinguished from each other only under transient conditions using very sensitive spectroscopy.
2. The Ce³⁺ formation is involved in the rate determining step of low-temperature CO oxidation over Pt/CeO₂ and Pt/Ce_{0.5}Zr_{0.5}O₂ catalysts. The much higher Ce³⁺ formation rate in a Pt/Ce_{0.5}Sn_{0.5}O₂ catalyst makes it more active for low temperature CO oxidation than Pt/CeO₂ and Pt/Ce_{0.5}Zr_{0.5}O₂ catalysts. The Ce³⁺ formation rate in Pt/Ce_{0.5}Sn_{0.5}O₂ is even faster than the Ce³⁺ oxidation rate, yielding a different structure of the active site during catalytic reaction.
3. Not only the redox activity of cerium in ceria-based catalysts determines the rate determining step of low temperature CO oxidation. For Cu-doped ceria, the reduction rate of Cu²⁺ to Cu⁺ better correlates with the overall CO oxidation rate, while the rate of Ce⁴⁺ to Ce³⁺ transformation is slower.

4. An initially high concentration of Ce^{3+} in $\text{Pt/Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (and probably other ceria-based catalysts) induced by reductive pre-treatments accelerates CO oxidation via an additional stoichiometric mechanism involving CO and O_2 and irreversible transformation of Ce^{3+} to Ce^{4+} .

Conclusions

We demonstrated that the combination of transient kinetics with highly sensitive time-resolved X-ray spectroscopy is a powerful approach for understanding reaction mechanisms and can potentially be applied to a large variety of heterogeneous catalysts. The information provided by spectroscopic methods allows defining strategies for the rational design of more powerful catalysts.

References

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