CO Oxidation

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Catalytically Active and Spectator Ce^{3+} in Ceria-Supported Metal Catalysts[**]

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Abstract: *Identification of active species and the rate-determining reaction steps are crucial for optimizing the performance of oxygen-storage materials, which play an important role in catalysts lowering automotive emissions, as electrode materials for fuel cells, and as antioxidants in biomedicine. We demonstrated that active Ce^{3+} species in a ceria-supported platinum catalyst during CO oxidation are short-lived and therefore cannot be observed under steady-state conditions. Using time-resolved resonant X-ray emission spectroscopy, we quantitatively correlated the initial rate of Ce^{3+} formation under transient conditions to the overall rate of CO oxidation under steady-state conditions and showed that ceria reduction is a kinetically relevant step in CO oxidation, whereas a fraction of Ce^{3+} was present as spectators. This approach can be applied to various catalytic processes involving oxygen-storage materials and reducible oxides to distinguish between redox and nonredox catalytic mechanisms.*

Oxygen-storage materials play an important role in automotive three-way catalysis,[1] carbon monoxide oxidation, and water-gas shift reaction,[2,3] electrode materials for fuel cells,[4,5] antioxidants in biomedicine,[6,7] solar thermochemical and photocatalytic water and carbon dioxide splitting.[8,9] However, the nature of active species responsible for these outstanding properties typically remains unknown. This is mainly due to the low concentration of active species and the necessity to distinguish them from inactive spectators, which requires direct spectroscopic identification of intermediates and quantitative comparison of their kinetic behavior to the global reaction rate.[10,11] The best catalysts for low-temperature CO oxidation, which are important for lowering automotive emissions, contain metal nanoparticles such as platinum, gold, and palladium supported on or promoted by metal oxides that demonstrate reducibility and oxygen-storage capacity (OSC), such as ceria, titania, and iron oxides.[12–17] Catalytic oxidation on such catalysts is simple only at first glance. It often remains unclear how oxygen molecules are activated, whether lattice oxygen is directly involved in the catalytic cycle, and if the catalytic mechanism is of redox type. A transient infrared spectroscopy study combined with density functional theory (DFT) calculations showed that during low-temperature CO oxidation on titania-supported gold nanoparticles oxygen activation takes place at the metal–support interface, whereas adsorbed CO is delivered by neighboring titania.[12] Moreover, recent kinetic and infrared spectroscopy experiments combined with DFT calculations demonstrated that oxygen from the titania support is not directly involved in the rate-determining step of CO oxidation on the Au/TiO_2 catalyst at room temperature. Instead, weakly adsorbed water is involved in the rate-determining step.[16] These results raise questions whether this type of associative rather than redox mechanism of low-temperature CO oxidation can also be valid for other reducible oxides and supported metals, and whether OSC is generally needed for low-temperature CO oxidation.

Ceria-based materials are classical oxidation catalysts used in automotive industry.[18] Addition of ceria increases the activity of metal nanoparticles for low-temperature CO oxidation, lowers the apparent activation energy, makes the reaction order in CO positive, and decreases the reaction order in oxygen.[2,19] Oxygen adsorption and activation preferentially occur on ceria and thus its competition with CO for adsorption sites on the metal nanoparticle is bypassed. Kinetic CO oxidation studies performed on ceria-supported platinum, palladium, and nickel nanoparticles showed that the rate of CO oxidation depends only on the length of the metal–ceria interface and that the rate is independent of the nature of the metal.[15] This finding underlines the major role of the ceria support in the activity of low-temperature CO oxidation catalysts; however, it does not explain the catalytic mechanism at the molecular level. The dynamics of oxygen uptake and release by ceria-based materials was intensively studied by in situ time-resolved methods including X-ray absorption spectroscopy (XAS), X-ray diffraction, pair-dis-

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tribution function, and infrared spectroscopy only above 200 °C.[20–22] These studies demonstrated that the rate of Ce^{3+} formation during redox cycling is greatly enhanced by the contact of ceria with metal nanoparticles. However, the rates of Ce^{3+} formation and consumption were never quantitatively correlated to the rate of any catalytic oxidation process; therefore it was never directly proven that Ce^{3+} is an active species. Here we demonstrate quantitative proofs on the formation of active Ce^{3+} species during CO oxidation on a platinum-promoted ceria-based catalyst even at room temperature. In addition, we show that a significant fraction of Ce^{3+} in the working catalyst does not participate in the catalytic cycle and can be considered as inactive spectators (Figure 1 a). To elucidate this, we applied time-resolved resonant X-ray emission spectroscopy (RXES), a technique that allows quantitative monitoring of the kinetics of formation and consumption of Ce^{3+} species in the working catalyst.[10]

We studied a 1.5 % Pt/CeO_2 catalyst containing 1.2 nm platinum nanoparticles supported on powdered ceria (Figure S1 in the Supporting Information). The catalyst was loaded into an in situ plug-flow reactor cell[23] and pretreated in 1 % H_2 at 150 °C to reduce platinum nanoparticles, as confirmed by Pt L_3-edge X-ray absorption near-edge structure (XANES) (Figure S2). The steady-state CO conversion rate was measured in 1 % CO and 4 % O_2 in argon at 24, 31, 38, and 44 °C at a constant flow (50 mL min^{-1}, corresponding to a space velocity of 600 mL h^{-1} g^{-1} for CO) making sure that CO conversion did not exceed 35 %. The experiments were performed only under lean conditions (excess of oxygen); however, it was previously demonstrated[15] that kinetics and mechanism of CO oxidation on ceria-supported metal catalysts should be very similar for lean, stoichiometric, and rich conditions. During transient experiments, we switched the oxygen supply on and off using fast solenoid valves, while maintaining the same total flow and 1 % CO concentration in argon. Under transient conditions platinum nanoparticles remained metallic and were always covered by CO, as confirmed by Pt L_3-edge XANES (Figure S2 b). If oxygen from ceria participates in CO oxidation, then once the oxygen supply is switched off the Ce^{3+} concentration should increase due to consumption of lattice oxygen. To quantify changes in the Ce^{3+} concentration, we continuously measured in situ RXES spectra of cerium with the 1 s repetition rate. We repeated the same experiment 80 times, periodically switching the gas-phase composition, and averaged the resulting spectra. Figure 1 b–e shows the Ce^{3+} concentration measured under transient conditions using the RXES (Figure 2 a) and quantified by a linear combination fit of the reference spectra (Figure 2 b). The Ce^{3+} concentration in the reference spectra was determined by Ce L_3-edge XANES (Figure S3). The initial rate of ceria oxidation is at least ten times higher than that of reduction, which explains why active Ce^{3+} species are short-lived and cannot be observed under steady-state conditions (Figure 1 a). It is interesting that Ce^{3+} does not completely disappear in oxygen-rich conditions, indicating the presence of Ce^{3+} spectator species uninvolved in the catalytic process. We assume that these Ce^{3+} species form

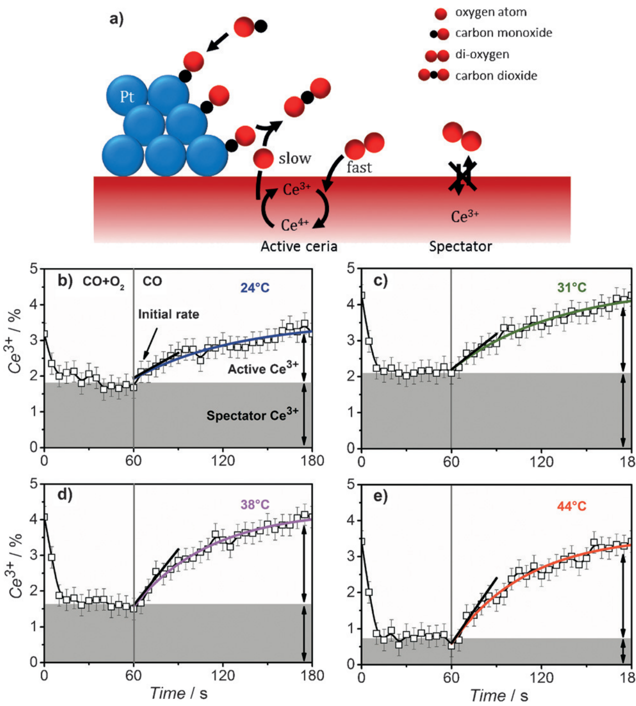

Figure 1. a) Representation of oxygen uptake and release by ceria during the CO oxidation cycle on a Pt/CeO_2 catalyst. In the slow part of the cycle, an oxygen atom from ceria at the Pt–CeO_2 interface reacts with CO adsorbed on platinum to afford CO_2, an oxygen vacancy, and two Ce^{3+} species. The fast part of the cycle involves CO readsorption on platinum and oxygen activation on ceria resulting in healing of the oxygen vacancy and oxidation of active Ce^{3+} species. Ce^{3+} spectator species do not participate in CO oxidation. b–e) Transient Ce^{3+} concentrations in the Pt/CeO_2 catalyst measured with RXES during cycling between 1 % CO + 4 % O_2 (0–60 s) and 1 % CO (60–180 s) gas mixtures at 24, 31, 38, and 44 °C. The increase in Ce^{3+} concentration in 1 % CO was fitted by an exponent function and the initial rate at the moment of switch (60 s) was determined (indicated as the slope). The concentrations of active and spectator Ce^{3+} species are indicated by arrows.

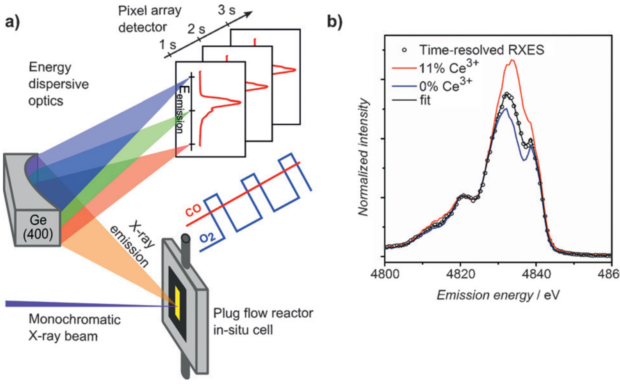

Figure 2. a) Experimental setup: The sample in the plug-flow reactor cell is excited by a 0.1 × 0.1 mm^2 monochromatic X-ray beam at 5.722 keV (4.5 eV below the Ce L_3 absorption edge of CeO_2). The Ce $2p_{3/2}3d_{5/2}$ RXES spectra were collected with 1 s repetition rate by an energy-dispersive X-ray emission spectrometer. b) Linear combination fit of time-resolved RXES spectrum (empty circles) using the reference samples containing 11 % Ce^{3+} (red curve) and 0 % Ce^{3+} (blue curve).

during the standard pretreatment of the catalysts in 1 % H_2 at 150 °C. Our experiment cannot distinguish between surface and bulk Ce^{3+}. During the catalyst pretreatment in hydrogen we observe the formation of 11 % of Ce^{3+}, which corresponds to an equivalent of 0.6 oxygen monolayers removed from the ceria surface.[24] Depth profiling experiments[25] by in situ high-energy XPS in a hydrogen atmosphere at similar mild conditions indicate that oxygen vacancies form only in the uppermost ceria layers. For these reasons, we suggest that spectator Ce^{3+} species are most probably located at the surface or in the near-surface bulk region of ceria. The oxidation of these species has a higher activation barrier than the oxidation of active Ce^{3+} species; therefore, they remain during CO oxidation at low temperature. The observation of Ce^{3+} is thus not necessarily related to catalytic activity.

We fitted the changes in Ce^{3+} concentration between 60 s and 180 s (Figure 1 b–e) by a single exponential decay function (see the Experimental Section in the Supporting Information) and determined the initial rate of Ce^{3+} production at the moment of the switch (60 s). To verify whether Ce^{3+} is a kinetically relevant intermediate in a redox-type mechanism, we compared the initial rate of its formation under transient conditions with the steady-state CO conversion rate. According to the equation,

$$2\,Ce^{4+} + O^{2-} + CO \rightarrow 2\,Ce^{3+} + V_o + CO_2, \qquad (1)$$

in which O^{2-} is lattice oxygen and V_o is an oxygen vacancy in the ceria structure, the rate of CO oxidation and CO_2 formation equals half that of Ce^{3+} production. Accordingly, we estimated the initial rates of CO_2 formation over a Pt/CeO_2 catalyst under transient conditions from RXES experiments and compared them with the steady-state CO_2 formation rates measured by gas chromatography. The results are presented in the Arrhenius-type plot in the Figure 3 and summarized in Table S1 in the Supporting Information. The fact that the CO_2 production rate is proportional to the Ce^{3+} formation rate was confirmed by online mass-spectrometric data (Figures S4 and S5).

The similarities between the rates and the activation energies directly prove that Ce^{3+} is an active species in CO oxidation. Moreover, it shows that Ce^{3+} formation is involved in the rate-determining step of this catalytic process proving the redox mechanism[10] explained in Figure 1 a. The apparent activation energy of CO oxidation determined in our work (36–44 kJ mol^{-1}) corresponds well to the literature values of 40–60 kJ mol^{-1} determined under steady-state conditions at 40–80 °C for CO oxidation on well-defined platinum nanoparticles supported on CeO_2.[15] Under similar reaction conditions, the pure ceria support did not show activity below 120 °C. This excludes that active Ce^{3+} species can be formed in the absence of platinum in a low-temperature range. The turnover frequency (TOF) of CO conversion per active site of Pt also corresponds well to the literature data. If we assume that active platinum atoms are situated at the Pt–CeO_2 interface (perimeter and corner sites),[15] which corresponds to 23 % of platinum atoms in the 1.2 nm nanoparticles, then the TOF can be defined as an activity per each of these sites. Extrapolating the TOF of our 1.5 % Pt/CeO_2 catalyst measured at 24–44 °C to 80 °C results in a TOF of 0.45 s^{-1}. This value is similar to the reported TOF of 0.2 s^{-1} for small platinum nanoparticles on ceria[15] and to a TOF of 0.3 s^{-1} for atomically dispersed platinum on FeO_x[13] at 80 °C and is much higher than a TOF of 3.8×10^{-4} s^{-1} for atomically dispersed palladium on alumina at 70 °C.[26]

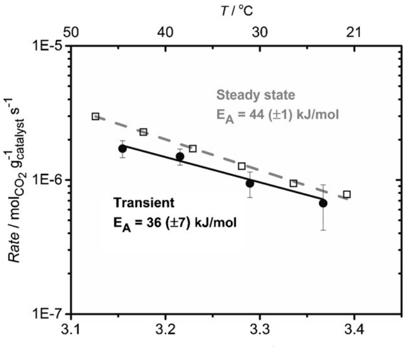

Figure 3. Arrhenius-type plot showing the CO_2 formation rates calculated from RXES experiments under transient conditions (filled circles and solid line) together with the steady-state CO_2 formation rates determined by gas chromatography (empty squares and dashed line).

The active site represents an ensemble of atoms performing the catalytic cycle. In our case, the active site should involve at least one oxygen atom, two cerium atoms and a platinum atom providing CO. The single exponential fit of the kinetics of Ce^{3+} formation under oxygen lean conditions (Figure 1 b–e) suggests that all active oxygen atoms that can be removed from Pt/CeO_2 within 120 s have the same activity and can be removed with similar activation energy. During each catalytic cycle, one of these oxygen atoms reacts with CO to form CO_2. We define the quantity of oxygen atoms that may participate in the reaction as the catalytically relevant OSC and the corresponding quantity of Ce^{3+} as the active cerium species (Figure 1 b–e). It should be emphasized that under steady-state conditions active cerium atoms are mainly present as Ce^{4+}, because the oxidation step of the catalytic cycle is much faster than the reduction step. The active Ce^{3+} species are short-lived and their specific role is to store electrons, which are needed for the activation of oxygen. The concentration of active cerium slightly increases with the increase of temperature (Table S1). It is interesting to understand where active cerium and oxygen species are located. Oxygen atoms at the Pt–CeO_2 interface should be more reactive than regular oxygen atoms on the ceria surface due to the close vicinity of CO adsorbed on platinum. Oxygen atoms at the Pt–CeO_2 interface should have a higher probability to react with CO than regular oxygen atoms on the ceria surface due to the close vicinity of CO species adsorbed on platinum. If we assume that each active platinum atom at the Pt–CeO_2 interface (perimeter and corner sites) is in contact with one active oxygen atom from ceria,[15] then the corresponding fraction of active cerium atoms would be about 0.6 %. A comparison of this model value with the experimental fraction of active cerium atoms (2–3 %) allows us to speculate that only oxygen and cerium and atoms very close to the metal–support interface are involved in CO oxidation at low temperature.

The exceptional performance of ceria-based materials in catalysis, fuel cells, and biomedicine is often explained by unique redox properties, the presence of oxygen vacancies and Ce^{3+} species.[6,7,18] However, Ce^{3+} that one observes with classical in situ methods under working conditions are not always active species but can be irrelevant spectators, whereas active species can be short-lived and practically invisible. The oxygen-storage capacity is generally considered as a crucial parameter for the activity of ceria-based catalysts. Our results indicate that the performance of the low-temperature CO oxidation catalysts rather correlates to the rate of Ce^{3+} formation than to the overall OSC. Therefore, more efficient catalysts can be rationally designed using materials with faster Ce^{3+} formation rate. The results suggest that the active Ce^{3+} species is short-lived and can be spectroscopically observed only under transient conditions. The transient spectroscopic method used in our work can be applied to other catalysts based on reducible oxides to determine whether the redox activity of an oxide is directly involved in the reaction cycle.

Keywords: ceria · CO oxidation · kinetics · time-resolved studies · X-ray spectroscopy

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