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A structural view of Pd model catalysts : high-pressure surface X-Ray diffraction

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Appendix A

On the possible hyperactivity of metal surfaces for CO oxidation

This appendix covers part of the ongoing discussion about active surface phases and the role of oxide for CO oxidation on Pd. The discussion arose as a result of the apparently irreconcilable difference between STM and SXRD measurements [23, 51, 91, 105] and PM-IRAS measurements [73, 134–136]. A consistent interpretation of our SXRD and STM data and the PM-IRAS results of Goodman is presented.

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Recently, Goodman and co-workers [73, 134–136] have challenged our interpretation [23, 51, 91, 105] of catalytic CO oxidation at atmospheric pressures, namely that at high O₂/CO pressure ratios Pd and Pt surfaces switch from a metallic structure to a surface oxide with a higher catalytic activity. On the basis of turnover frequencies (TOFs) and polarization modulation infrared absorption spectroscopy (PM-IRAS), Goodman et al. claim that an intermediate metallic phase dominated by chemisorbed oxygen is chemically even more active. In this comment we provide a natural, alternative explanation for the observations in refs [73, 134–136], which we support with new TOF data and structural measurements obtained with surface x-ray diffraction (SXR).

In refs [73, 134–136], metal crystals were heated inside a large batch reactor, filled with an O₂/CO mixture. Figure A.1 reproduces Figure 5 of ref [73], showing the TOF on Pd(100), obtained from the decay rate of the total pressure for several initial O₂/CO ratios. Consistent with our scanning tunneling microscopy (STM) [51, 91, 105] and SXR [23] observations, the low temperature branches in Fig. A.1 are identified in ref [73] as the regime where Pd(100) is metallic with adsorbed CO and O [51]. The TOF increased with temperature up to a plateau, which is taken as the signature of a mass-transfer limited regime, in which the flux of CO molecules diffusing to the surface directly determines the observed TOF. Our observations had shown such plateaus to concur with the presence of an oxide at the surface and we had argued that this would change the reaction mechanism [23, 51, 91, 105].

The arrows indicate transient peaks in reaction rate, occurring immediately before the TOF settled at the plateau and showing that temporarily Pd(100) was able to convert more CO than the mass-transfer limit of the plateaus. In ref [73], this is taken as evidence for an intermediate surface structure. The PM-IRAS data show no signal from adsorbed CO during the TOF peaks from which ref [73] concludes that the intermediate structure should be metallic Pd(100) with an O-dominated adsorption layer.

In Fig. A.1b, we have repeated these TOF measurements in a flow-reactor setup [78] that combines mass spectrometry and SXR. Our results were obtained under steady-state conditions with the temperatures and O₂/CO ratios carefully following those in Fig. A.1a. In Fig. A.1b, all plateaus are at the same TOF since we added argon to keep the total pressure constant, thereby keeping the diffusion coefficient of CO through the gas mixture at the same value for all O₂/CO ratios. Transient peaks are absent under the steady-state conditions of Fig. A.1b;

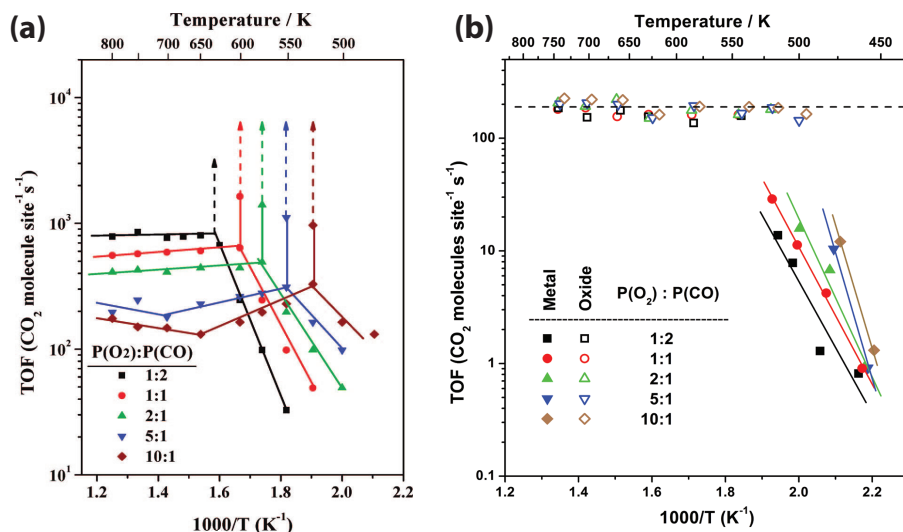


Figure A.1: **a)** Arrhenius plots of the CO₂ formation rate measured by Gao et al. [73] for several O₂/CO mixtures over Pd(100), each mixture starting from an initial CO partial pressure of 8 Torr. Transient reaction rate jumps are indicated with arrows. Data reprinted from ref. [73]. **b)** Equivalent data set, measured in a flow reactor-SXRD setup. The CO pressure was 8 Torr for all ratios, but argon was added to the gas mixture to keep the total pressure constant at 152 Torr. The surface structure was determined simultaneously with the reactivity by surface x-ray diffraction. Open symbols denote where the SXRD measurements showed the presence of an oxide (surface oxide, bulk oxide, or powder pattern) and solid symbols indicate under which conditions SXRD measured an oxide-free metal surface.

they only occur during the transition from metal to oxide, as was the case in Fig. A.1a. We note, that transient peaks have also not been observed in any of the measurements of refs [73, 134–136] in the reverse direction, when the oxide was reduced. Our SXRD measurements identify the structure of the Pd(100) surface at each of the conditions in Fig. A.1b. We have resolved a variety of oxide structures at detailed account of which is provided in Chapter 3; in Fig. A.1b all oxide structures are indicated by open symbols. The solid symbols are for conditions where all Pd atoms were on regular Pd lattice positions, that is, for a metallic surface. We see that the oxide and metal structures separate in a very simple way; all cases with a mass-transfer limited TOF correspond to an oxide,

while all lower-temperature observations of temperature dependent TOF values correspond to metallic Pd(100). In search for an intermediate structure, we have driven the surface many times through the metal-oxide phase transition by changing either the temperature or the O₂/CO ratio. Using a pixel camera, the time for the SXRD structure identification was reduced to 1 s and even at this time scale we find the increase in TOF to correlate with the appearance of an oxide without any sign of an intervening structure.

We suggest an alternative explanation for the transient TOF peaks. In the limit of zero reactivity, the concentration profile of CO in the reactor is completely flat, while in the limit of infinite reactivity, there is a strong gradient with a zero local CO concentration at the surface. Therefore, when the surface switches from slow to fast CO consumption, the concentration profile must change from a weak to a strong gradient. This naturally leads to transient TOF behavior, precisely of the type in refs [73, 134–136]. As long as the new profile has not been established fully, the CO concentration in the gas close to the surface has not yet reduced fully to its new, lower value and the flux of CO impinging and reacting to CO₂ is exceedingly high. The excess TOF over the full transient adds up to the reduction in total amount of CO in the reactor between the profiles before and after the switch. This scenario not only explains the transient peaks when switching from a low to a high TOF, but also the absence of transient peaks in the reverse direction. Then, the CO concentration near the surface is initially lower than the appropriate concentration for the new, lower-reactivity metal phase, so that a negative transient should occur with an even lower TOF. Within the experimental noise, the TOF-plots in refs [73, 134–136] are fully consistent with this.

The duration of the transient peaks reflects the settling time for the new profile, which is either dictated by the system's mass-transfer properties or by the intrinsic reactivity of the catalytic surface. We estimate that in refs [73, 134–136], the characteristic diffusional mass-transfer time should be below 1 s. The significantly longer durations observed, for example, 8 s in Figure 11 of ref [73], suggest that they stem from the combination of the high surface reactivity of the newly formed oxide, the significant overshoot in temperature resulting from the reactivity jump, and the correspondingly strong convective gas flow.

Finally, we compare the PM-IRAS observations of adsorbed CO, which Goodman and co-workers used to obtain information on the catalyst's surface structure, with direct SXRD. When the TOF was low and temperature-dependent, PM-IRAS showed CO adsorbed in bridge sites on metallic Pd(100), consistent

with our SXR D observation of a well ordered metal surface. Under most gas mixtures at higher temperature, during the transient TOF-peak and on the subsequent plateau, no adsorbed CO was detected in the infrared spectra, indicating high catalytic activity. Figure A.1b shows oxidic surfaces under all these conditions. Low CO coverages have been found on oxidized Pt particles in the in situ measurements of [117]. Only for highly oxygen-rich mixtures infrared signals of CO returned, characteristic for CO on bulk PdO [73] Under these conditions, SXR D showed a polycrystalline, bulklike PdO film, whereas we found epitaxial surface oxide structures under less oxygen rich conditions. We speculate that each of the oxides formed on Pd(100) has a different reactivity, in most cases beyond the mass-transfer limit, and that the bulk-like PdO is less active than the other oxides.

We conclude by pointing out that our own experimental findings and our interpretation of the PM-IRAS results, including those concerning the low CO coverage on the surface oxide, closely agree with recent kinetic Monte Carlo calculations with energies derived from DFT calculations [71].

