

# Comment on “Catalytic Activity of the Rh Surface Oxide: CO Oxidation over Rh(111) under Realistic Conditions”

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In their most recent publication, Gustafson et al.<sup>1</sup> suggest the importance of a surface oxide phase for high CO<sub>2</sub> formation in CO–O<sub>2</sub> reactions. However, a close inspection of their data in Figure 2 of their paper shows clearly that the surface oxide phase, formed under O<sub>2</sub>/CO-rich reaction conditions, contributes negligibly to CO<sub>2</sub> formation. At the reaction time of 1200 s (~230 °C) in Figure 2b, a sudden increase in the CO<sub>2</sub> formation rate is apparent while the SXR D feature in Figure 2d, corresponding to the surface oxide phase, is at most barely detectable. Obviously, during the rapid increase in the CO<sub>2</sub> formation rate between 170 and 230 °C, the catalytic surface corresponds to reduced (metallic) Rh, not an oxide phase.

From reaction time 1200 to ~2500 s, the SXR D feature of the surface oxide phase intensifies and saturates (Figure 2d) while the CO<sub>2</sub> formation rate remains essentially constant (Figure 2b). As shown and discussed extensively in our previous publications,<sup>2–6</sup> this plateau region in the reaction rate is due to mass transfer limitations. That is, an increase in the temperature has no effect on the CO<sub>2</sub> formation rate, since the rate is now entirely limited by the arrival of CO, the limiting reagent in an oxygen-rich reactant environment (by oxygen-rich, we are referring to O<sub>2</sub>/CO reaction mixtures greater than the stoichiometric ratio). The consequence is that within this plateau region for oxygen-rich reaction mixtures, the near-surface gas phase composition is essentially pure O<sub>2</sub>. Obviously, heating Rh in pure oxygen to *T* = 230 °C and above will lead to the formation of surface Rh oxide, as is indicated by the SXR D data of Figure 2.

The authors conclude that the rate within the plateau of Figure 2b is due to reaction catalyzed by the surface Rh oxide. As pointed out by us previously,<sup>7</sup> this is an incorrect conclusion. Within the so-called “oxide” region (plateau region) and with an increase in the temperature, a proportionally smaller fraction of the total surface in the reduced metallic form is required to sustain the CO<sub>2</sub> formation rate in this mass transfer limited regime. For example, at *T* = 300 °C less than 1% of the surface sites need be in the reduced state to account for the CO<sub>2</sub> conversion at the rate measured in the plateau region.

As the temperature is reduced in the data of Figure 2 (from ~2500 s and above), the oxide is maintained until ~230 °C and the reverse behavior of that seen during the temperature increase is observed. Again, this is simply because the oxide is reduced to the metallic state with the reaction regime following a normal Arrhenius behavior.

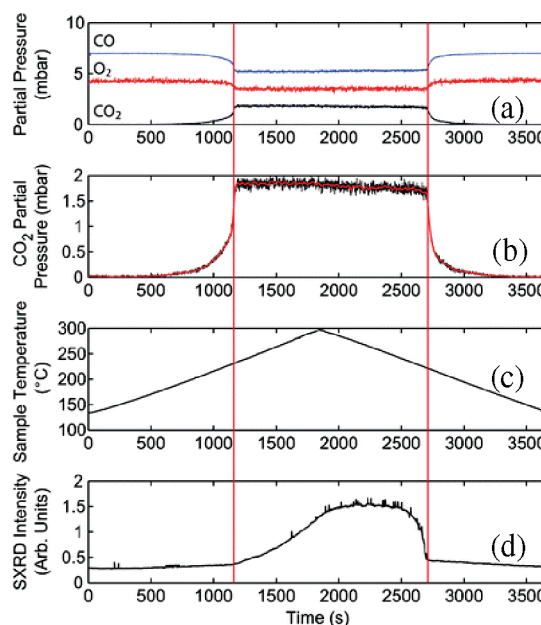


Figure 2. From Gustafson et al.<sup>1</sup>

As for the results shown in Figure 3 (shown below) of the authors' paper, the correct interpretation is obvious in view of our earlier data previously discussed in detail.<sup>2–6</sup> For a stoichiometric reaction mixture (Figure 3c), the rate data display Arrhenius behavior until the rate reaches the mass transfer limit. We note that the mass transfer limit in the present study is considerably restricted (TOF ~ 25) by the overall pressure (due to the He makeup gas used to bring the overall pressure to 500 mbar) whereas in our previous studies, where no makeup gas was used, the mass transfer limit (turnover frequency (TOF) or CO<sub>2</sub> molecules produced per surface site per second) achieves a value of ~1000. This effect is related solely to the lower total pressure of the reactants, allowing higher rates to be measured. This is important to note in that the ability to “see” the so-called hyperactive states (reaction rate “jump”) found in our previous studies<sup>2–5</sup> is facilitated by having a pure reactant boundary layer and a relatively low reactant pressure to minimize mass transfer limitations and thereby maximize the measurable rate. In any case, the authors' data do, in fact, show a limited “jump” in the rate for oxygen-rich reactant conditions in Figure 3a,b; this is observed where the reaction rate deviates from the Arrhenius red line, prior to the mass transfer “plateau” region. These rapid rises in the rate indicate the approach to the mass transfer limit, where the reactant mixture in the near surface region becomes increasingly rich in oxygen, that is, starved of the rate-limiting reagent carbon monoxide. The CO<sub>2</sub> formation rate, in turn, responds to this rapid increase in the O<sub>2</sub>–CO ratio as predicted by our previous studies<sup>2</sup> with the rate rapidly rising to the mass transfer “plateau” region. We emphasize that this behavior, where the reaction rate rises (“jumps”) sharply with temperature, only occurs and is only possible in an oxygen-rich environment and is not exhibited by a stoichiometric or reducing reaction environment, as that found in Figure 3c of the authors' paper. We also note and reiterate that this “jump” of reaction rate in Figure 3b would correspond to the region of Figure 2d (before ~1200 s), which shows barely detectable SXR D oxide intensity.

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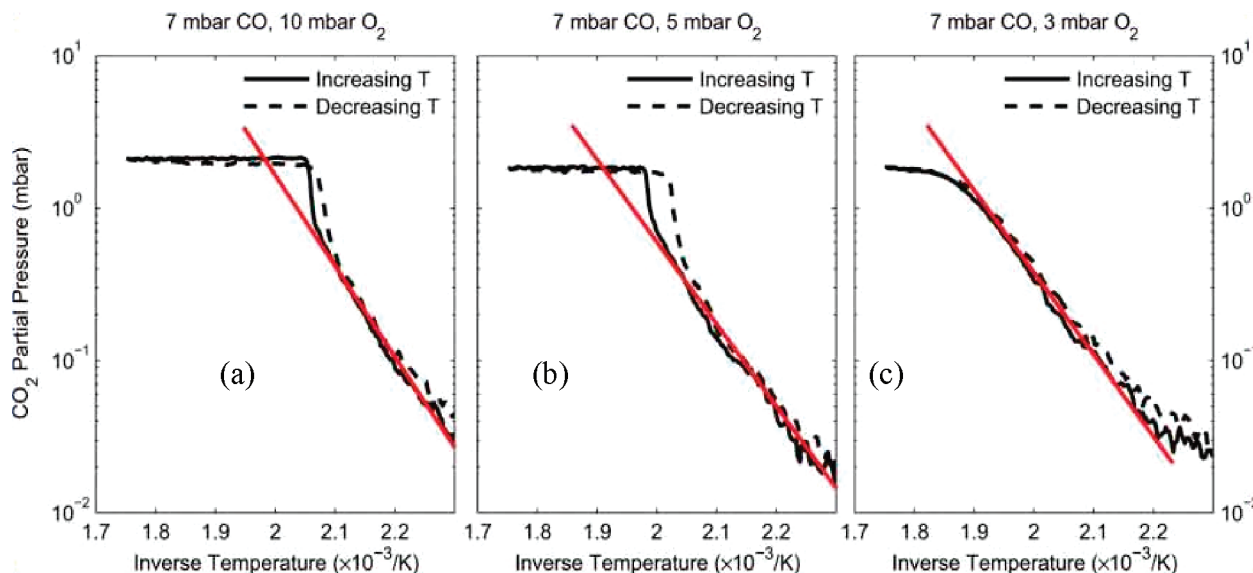


Figure 3. From Gustafson et al.<sup>1</sup>

We are in complete agreement with the conclusion of the authors that bulk Rh oxide “is inactive for CO oxidation” as we have previously contended. The authors amend their previous contention that the bulk oxide is indeed active and now “propose that the surface oxide present during these measurements is rich in defects and/or coexisting with patches of metallic surface, allowing for CO adsorption.” This is indeed the case, and as we have shown and argued in our previous extensive studies, the active phase is a reduced metallic surface essentially covered by a monolayer of chemisorbed oxygen atoms.<sup>2</sup> As discussed in the previous paragraph, the CO oxidation rate achieved during the mass transfer limited (“plateau”) regime, invariably is and can be related to the available sites remaining on the surface being oxygen-covered, reduced metallic Rh surface sites.<sup>7</sup> We emphasize that these sites are (1) regular surface sites and (2) CO-uninhibited. The CO-uninhibited reaction temperature regime can be reached by (1) increasing the O<sub>2</sub>/CO ratio of the reactants and/or (2) increasing the sample temperature to decrease the surface CO coverage. The CO-uninhibited surface, being no longer “protected” by CO, is easily oxidized to form a surface oxide and then further oxidized to the bulk oxide. The appearance of the surface oxide corresponds to the onset of the CO-uninhibited regime rather than to the appearance of an active phase. Following our argument, the more plausible explanation of the results of Figure 2 is that at a reaction time of 1200 s, the CO-uninhibited regime is reached as indicated by the dramatic reaction rate increase. With subsequent increases in temperature, the surface is gradually oxidized and the surface oxide SXR signal gradually increases. Clearly, however, the residual rate can be accounted for by the reduced metal sites remaining, since only a very small fraction (<1%) of these surface sites are required to account for the mass transfer limited CO<sub>2</sub> formation rate.

In discussing the data of Figure 3 in their paper, the authors state that “it is clear that the surface oxide phase is more reactive than the CO covered metallic phase.” We emphasize that this comparison, and therefore this statement, is entirely meaningless. A proper comparison is that between a metallic surface not poisoned by CO and a nondefective oxide surface. The result of the comparison is simple. The surface of Rh bulk oxide is essentially completely inactive whereas the reduced metal

surface can achieve CO–O<sub>2</sub> reaction probabilities approaching unity in the absence of mass transfer limitations.<sup>2,5</sup>

Finally, in comparing CO oxidation kinetics on Pt-group metals at low and high pressure, it is important to note that the underlying causes of relative low rates is either CO-inhibition or O-inhibition, behavior entirely understood invoking the Langmuir–Hinshelwood mechanism. Accordingly, the only successful strategy to improve the reactivity of a CO oxidation catalyst is to eliminate these two inhibition effects. We have shown recently<sup>8,9</sup> that a Pd–Au alloy displays much higher reactivity than pure Pd at low temperatures toward CO oxidation at elevated pressures. The major cause has been identified to be a much reduced binding of CO to the Pd–Au surface. This argument also explains the anomalous behavior of Ru compared with other Pt-group metals in CO oxidation, namely, the much higher reactivity of Ru at relatively low temperatures is simply because this metal reaches the CO-uninhibited regime at lower temperatures compared with the other noble metals.<sup>10</sup> On the other hand, Rh displays stronger O-inhibition than Pd and Pt. At elevated temperatures this metal has lower reactivity than Pd and Pt, both at low and high pressures.<sup>3–5</sup>

In summary, the authors’ data are entirely in agreement with and are completely predicted by our previous data discussed in refs 2–6. These have been and can only be interpreted accurately assuming that the oxides of noble metals, both surface and bulk oxides, are many orders of magnitude less reactive in the CO-uninhibited region compared to an oxygen-covered reduced metal surface.

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