Reply to “Comment on CO Oxidation on Pt-Group Metals from Ultrahigh Vacuum to Near Atmospheric Pressures. 2. Palladium and Platinum”

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First of all, it is essential to clarify the terms “reactive phase” and “most reactive phase” since the central point of all the arguments in the Comment is the relative reactivity of various phases. The most reactive phase would clearly be that phase upon which the impinging CO and O2 molecules achieve a reaction probability of unity or near unity. The classical molecular beam work by Ertl and co-workers\(^1\)–\(^3\) has demonstrated that under optimum conditions, a reaction probability of near-unity is obtainable on metallic Pt and Pd surfaces. In contrast, a reaction probability even remotely close to the CO/O2 collision limit has never been achieved on any oxidized phase.\(^2\),\(^4\)–\(^6\) These results in themselves constitute a self-proof that an oxide phase is much less reactive than a metallic phase.

In the paper to which the Comment is addressed, the Pt and Pd surfaces that exhibited the highest CO2 formation rates (TOFs) were those observed to be metallic, covered with a full layer of chemisorbed oxygen and an undetectable amount of CO at reactant pressures of \(\leq 10^{-3}\) Torr. In other words, the most highly reactive phase of unsupported Pt and Pd catalysts is invariably a metallic surface.

If collision-limited reaction rates could be achieved on the most highly reactive surfaces at realistic catalytic pressures, reaction rates or TOFs would reach \(\sim 10^7\) CO2 molecules site\(^{-1}\) s\(^{-1}\).\(^7\) Of course, these rates are never reached in reality because of mass transfer limitations, that is, the reaction rate is limited by the availability of reactant molecules in the near surface region. The reaction rate on planar catalysts, such as those used in the studies being discussed, can be enhanced by circulation of the reactants or by reducing the size of the catalyst.\(^7\),\(^8\) Such efforts invariably lead to enhanced TOFs to some extent (approaching \(\sim 10^4\) CO2 molecules site\(^{-1}\) s\(^{-1}\) with the experimental setup described in ref \(8\)). This is to say, metallic surfaces outside the CO-inhibited regime are capable of reaching extremely high TOFs and the so-called “jump” points shown in Figure 1a of the Comment are manifestations of this behavior. Whether or not this jump behavior is observed depends critically on the CO supply in the near surface region and to a large extent on the experimental reactor configuration.

In any case, the explanation of the results observed in Figure 1b of the Comment of van Rijn et al. is rather straightforward. In the mass transfer limited regime (TOF \(\sim 10^7\) CO2 molecules site\(^{-1}\) s\(^{-1}\)), the number of highly active sites (sites that are capable of achieving TOF \(\sim 10^7\) CO2 molecules site\(^{-1}\) s\(^{-1}\)) required to consume the available CO is an extremely small fraction of the total number of surface sites. For example, for a TOF of \(10^5\), only \(\sim 0.01–0.001\)% of active surface sites would be required. SXRD is a technique that determines the structure of the majority surface phases whereas the observed reaction rate can be easily sustained by only a very small fraction of the total surface sites. For a reaction dominated by minority sites, SXRD is not an appropriate technique to “see” the nature of the active site nor can it be expected to correlate the active structure with the reaction kinetics measurements.

It is also noteworthy that the kinetic data of Figure 1b in the Comment of van Rijn et al. are questionable particularly in the CO-inhibited regime given that numerous previous studies have shown that the CO2 formation is approximately \(+1\) order with respect to O2 and \(-1\) order with respect to CO.\(^4\),\(^5\),\(^9\),\(^10\) This behavior is clearly not exhibited by the data in Figure 1b.

In summary, the most reactive phase of Pt and Pd at low and high pressures is identical and corresponds to the reduced metal. At pressures, for example, \(< 10^{-5}\) mbar, such surfaces under optimal reactant conditions exhibit collision-limited reactivities. However, at elevated pressures, for example, \(> 10^{-5}\) mbar, collision-limited reaction is not possible due to mass-transfer limitations. Also because of mass-transfer limitations, the most reactive phase can quickly become oxidized at reaction conditions outside the CO-inhibited regime. Within this mass-transfer limited regime, the oxide phases so formed do not contribute significantly to the observed reactivity, but rather the residual activity arises primarily from a very small fraction of reduced or metallic-like sites.

References and Notes