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Structure sensitivity of CO oxidation over rhodium. Reply to comments by Fisher, Peden, Oh and Goodman

Michael Bowker, Quanmin Guo, Yongxue Li and Richard W. Joyner
Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

We recently published a letter [1] where we drew attention to the structure sensitivity of CO oxidation at rhodium single crystal surfaces. Fisher, Peden, Oh and Goodman, (previous letter, hereafter referred to as FPOG) have commented on some aspects of our work, in particular claiming to have noted the phenomenon of structure sensitivity in this reaction in previous studies [2–5]. They also criticise certain aspects of our interpretation.

The clear message from the studies of FPOG is that CO oxidation is *structure insensitive* on rhodium and this is demonstrated by these extracts from the *abstracts* of their papers:

"*The CO/O_2 reaction was found to be insensitive to the structure of the surface*, as evidenced by the *identical rates, activation energies and partial pressure dependencies* measured on the two single crystal surfaces" [Rh(111)and(100), ref.[3], our italics].

"The specific rates and the partial pressure dependencies determined for the single crystals are in excellent agreement with results obtained previously for high surface area supported catalysts, *demonstrating the structure insensitivity of this reaction*" [ref. [5], our italics].

"...the kinetics of the CO–NO reaction, *unlike the CO/O_2 reaction kinetics*, are sensitive to changes in the catalyst surface characteristics" [ref.[2], our italics].

In none of their abstracts do they mention the *structure sensitivity* of the reaction, so it is not appropriate for FPOG to claim that they said that the CO oxidation reaction was structure sensitive all along. The objective of our letter was to show that the reaction is unequivocally structure sensitive under some conditions, and to delineate and explain these. We did state, incorrectly, that CO oxidation results from single crystal planes had not been directly compared previously; we recognise that FPOG did make such a comparison and we apologise for our error.

The FPOG papers together represent a valuable study of CO oxidation and evidence is presented which shows structure sensitivity under some conditions, however the authors largely ignore or misinterpret this. Ref. [3] claims that the reaction is structure insensitive, while noting some deactivation at high oxygen pressures which is suggested to be due to the formation of Rh_2O_3 and to enthalpy of formation differences of the *bulk* oxide on different rhodium surfaces. In similar vein, ref. [4] includes a single paragraph comparing results on Rh(111) and (100), and a single figure which shows that the reaction is structure sensitive under one set of conditions, (fig. 8). There is no discussion of this observation nor is there any consideration of its possible generality. It is the essence of our paper that structure sensitivity is observed when CO desorption is not rate limiting and can occur *when less than a monolayer of chemisorbed oxygen is present*. It is a strength of our experimental approach that rates of reaction and surface coverages are directly measured together.

We accept that the last word has not yet been said on the detailed kinetic modelling of this reaction, and recognise that both our model [6] and that of Oh, Fisher, Carpenter and Goodman [2] have deficiencies. In constructing our model we used experimental data as far as possible, but were forced to assume coverage independent preexponential factors. This is not entirely satisfactory, although the modelling of the results is reasonably good. By contrast, the model derived in ref. [2] makes assumptions about some input parameters which are simply incorrect. A value of 0.01 is assumed for the sticking coefficient of oxygen on clean Rh(111), while we have recently shown that sticking is much more effective, with a probability of 0.4 ± 0.02, almost independent of temperature [7]. There is clearly room for more modelling work.

We welcome the comments of Fisher, Peden, Oh and Goodman and are delighted that they now recognise the importance of structure sensitivity in this interesting reaction.

References

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