Catalysis Letters 22 (1993) 271–274

COMMENT

Comment on "Structure sensitivity in CO oxidation over rhodium" by M. Bowker, Q. Guo, Y. Li and R.W. Joyner

D. Wayne Goodman

Department of Chemistry, Texas A & M University, College Station, TX 77843-3255, USA

Charles H.F. Peden

Molecular Science Research Center, Pacific Northwest Laboratories, Richland, WA 99352, USA

Galen B. Fisher and Se H. Oh

Physical Chemistry Department, General Motors NAO Research and Development Center, Warren, MI 48090-9055, USA

In a recent letter [1], Bowker, Guo, Li and Joyner (BGLJ) note the structure sensitivity of CO oxidation with respect to Rh(111) and Rh(110), under conditions where the CO coverage is negligible and the oxygen coverage is high. Such structure sensitivity in the low CO coverage region has been noted and studied previously [2,3] in publications cited by BGLJ. Although cited, the authors apparently were not familiar with the contents of either reference. For example, BGLJ state in the introduction with respect to ref. [2] that "all data were obtained under conditions where the surface was covered by nearly a full layer of molecularly adsorbed CO." Furthermore, BGLJ close their introductory remarks with the statement "Surprisingly, there have been no studies in which the rates of reaction on different single crystal planes have been compared directly." Both of these statements are simply not true.

Ref. [2], the title of which is "Kinetics of CO oxidation by O_2 and NO on Rh(111) and Rh(100)", discusses in great detail the comparative rates of CO oxidation obtained at high (~ 1 atm) pressures over these two particular Rh surfaces. Similarly, Schwartz et al. [3] describe comparative rate measurements over the same Rh(111) and Rh(100) surfaces obtained at low (~ 10^{-7} Torr) pressures, generally the same pressure range studied by BGLJ [1].

Refs. [2,3] also both describe two kinetic regimes for the CO–O_2 reaction over Rh. In the first of these regimes the reaction is negative first order in CO pressure and positive first order in oxygen pressure. In this regime in ref. [2], CO oxidation rates over Rh(111) and Rh(100) surfaces are shown to be distinctly *structure insensitive* at conditions near stoichiometry. In ref. [3] this regime near stoichiometry occurs below 450 K, as it does for BGLJ [1]. The discussion in ref. [2] accounts for this behavior on the basis of a kinetic model developed previously by Oh et al. [4]. For reaction conditions near stoichiometry and at moderate temperatures, CO is the dominant surface species and CO desorption is required to provide adsorption sites for O_2 molecules, that then are able to dissociatively adsorb. *Importantly (see below), the subsequent Langmuir–Hinshelwood (LH) reaction between chemisorbed CO and O-atoms occurs rapidly with a relatively low activation energy* [4]. Structure insensitivity can then be attributed to the similar CO desorption energies from metal surfaces with variable surface atomic structure [5], as restated by BGLJ [1]. That the high pressure and low-pressure behavior in this kinetic regime is equivalent and accurately described by the same model, even for data taken over a pressure range of eight orders of magnitude, is clearly shown in ref. [3].

In contrast, both refs. [2,3] describe results that show the CO oxidation reaction becomes *structure sensitive* at high temperatures and/or high O_2 partial pressures. At low pressures in ref. [3] the CO–O_2 reaction rate in this regime is limited by the availability of CO and is *positive* order in CO and negative order in O_2. In both refs. [2,3], structure sensitivity results when the CO coverage is reduced due to CO desorption (higher temperatures) and/or competitive O_2 adsorption (higher O_2 partial pressures). Correspondingly, the oxygen surface coverage on Rh rises. Clear evidence for the correlation of these changes in surface coverages with changing reaction rates was presented in refs. [2,3], and was shown again by BGLJ [1]. However, we believe that the cause of structure sensitivity is likely to be different for the case of high-pressure reaction [2] compared to the results from low-pressure reaction [1,3]. Hence, the structure sensitive kinetic regimes at high and low pressures may *not* be directly equivalent. This belief is supported by the difference in the *relative* activities of the rhodium surfaces measured for the reaction conditions when structure sensitivity is observed. In the low-pressure experiments [1,3], the more open (100) and (110) surfaces are more active than close-packed Rh(111). At high ($\sim$ 1 atm) pressures, the order of reactivity is reversed with Rh(111) showing a higher activity at high O_2 partial pressures relative to Rh(100) [2]. The authors in ref. [2] interpreted this as due to the greater proclivity of the more open Rh(100) surface to oxidize compared to the relatively smooth Rh(111) surface. In fact, three-dimensional oxidation of Rh(111) has been shown to occur at high O_2/CO ratios for the CO oxidation reaction at temperatures greater than 500 K [6]. In contrast, previous studies have shown that Rh(111) will not bulk-oxidize at O_2 pressures as high as 10^{-5} Torr and temperatures up to 1000 K [7,8] even in the complete absence of CO.

BGLJ [1] attribute the greater activity of the Rh(110) surface relative to Rh(111) as being due to a difference in the activation energy for the LH reaction between chemisorbed CO-molecules and O-atoms on these two surfaces. This is only one of several possible explanations and, perhaps, the least likely. The rate of the LH reaction to form CO_2 can be taken to be of the form [4]

$$r_{CO_2} \approx A\, e^{(-E/R_gT)}\theta_{CO}\theta_O \equiv k_{CO_2}\theta_{CO}\theta_O\,.$$

As such, in addition to the LH activation energy, E, variations in the preexponential factor, A, and surface coverages of CO and O are, of course, important contributors to changing CO_2 formation rates. If we assume initially that A and E do not change on any particular Rh surface with changing adsorbate (CO and O) coverages, the maximum rate will still be determined by a delicate balance between the CO and O coverages, both of which are critically dependent on each other. For example, the presence of large oxygen coverages will certainly effect CO adsorption (sticking) and desorption kinetics. In fact, the measurement of the CO sticking coefficient as a function of oxygen coverage has been described [9]; on Rh(111) it decreases with increasing oxygen coverage [10]. Without in situ measurements of sticking probabilities and coverages of oxygen and CO on the relevant surfaces at reaction conditions, most assuredly nothing can be inferred from rate measurements regarding the relative activation barriers of CO oxidation on any two surfaces as suggested by BGLJ. Notably, BGLJ's citation of similar temperature-programmed desorption (TPD) curves for CO from fully CO-covered Rh(111) and Rh(110) is not particularly relevant to determining θ_{CO} on these surfaces when they are oxygen-covered and the CO coverage is low. Even in the absence of oxygen, θ_{CO} will, of course, depend on the *adsorption* as well as the *desorption* kinetics, and only the latter behavior is obtained in TPD experiments. With respect to the possibility that structure sensitivity results from structure sensitive LH activation energies, E, one should consider that the LH reaction rate constant, k_{CO_2}, is quite high and therefore, not likely to be rate-limiting. For example, when sufficient θ_O is present, virtually all coadsorbed CO will react to form CO_2 before the onset of CO desorption on Rh(111) [11]. Finally, it is worth mentioning that A can potentially be very sensitive to adsorbate structure by, for example, a change from mixed to segregated islands as a function of adsorbate coverages [4], and this might be expected to be structure sensitive as well.

In summary, previous work described in refs. [2,3] does directly compare $CO–O_2$ reaction rates on different single crystal planes of rhodium. This work also shows clearly that CO oxidation is structure sensitive on Rh in the low CO and high oxygen coverage regime as noted by BGLJ [1]. A determination of the mechanism for this structure sensitivity, particulary that observed in low pressure ($< 10^{-5}$ Torr) experiments, will require considerable additional study.

References

[1] M. Bowker, Q. Guo, Y. Li and R.W. Joyner, Catal. Lett. 18 (1993) 119.

[2] C.H.F. Peden, D.W. Goodman, D.S. Blair, P.J. Berlowitz, G.B. Fisher and S.H. Oh, J. Phys. Chem. 92 (1988) 1563.
[3] S.B. Schwartz, L.D. Schmidt and G.B. Fisher, J. Phys. Chem. 90 (1986) 6194.
[4] S.H. Oh, G.B. Fisher, J.E. Carpenter and D.W. Goodman, J. Catal. 100 (1986) 360.
[5] P.J. Berlowitz, C.H.F. Peden and D.W. Goodman, J. Phys. Chem. 92 (1988) 5213.
[6] C.H.F. Peden, P.J. Berlowitz and D.W. Goodman, in: *Proc. 9th Int. Congr. on Catalysis*, Vol. 3, eds. M.J. Phillips and M. Ternan (Chemical Institute of Canada, Ottawa, 1988) p. 1214.
[7] D.G. Castner and G.A. Somorjai, Appl. Surf. Sci. 6 (1980) 29.
[8] A.D. Logan, A.K. Datye and J.E. Houston, Surf. Sci. 245 (1991) 280.
[9] D.F. Padowitz, K.A. Peterlinz and S.J. Sibener, Langmuir 7 (1991) 2566.
[10] K.A. Peterlinz, PhD Thesis.
[11] T.W. Root, L.D. Schmidt and G.B. Fisher, Surf. Sci. 150 (1985) 173.