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Structure sensitivity in CO oxidation over rhodium

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The rates of CO oxidation on the (110) and (111) planes of rhodium have been directly compared using a thermal molecular beam reactor. When the surfaces are largely covered by CO the reaction rate is the same on the two crystal planes. At higher temperatures, where CO desorbs and the surface becomes oxygen covered, the reaction becomes structure sensitive, being markedly faster on the more open (110) plane.

Keywords: Rhodium; CO oxidation; single crystals; structure sensitivity; molecular beams

Rhodium is an important element in catalysts for treating pollution from mobile sources (for a review see ref. [1]) and is particularly effective in removing NO_x due to its good efficiency in dissociating NO. The resulting dissociated nitrogen adatoms undergo homonuclear recombination to N_2 and the oxygen is largely removed by CO as CO_2. Thus a detailed understanding of the CO oxidation reaction is of significance for designing better, more efficient catalysts which legislation periodically demands.

There are relatively few studies in which rhodium has been used as the catalyst, but perhaps the most significant have been the early work of White and co-workers [2–4], and more recent studies of Oh and co-workers [5,6] who found structural anisotropy in the rate of the CO/NO reaction, but complete structural insensitivity of the CO/O_2 reaction. They compared the reaction on a Rh(111) single crystal and on a Rh/Al_2O_3 catalyst at a total pressure of around 20 Torr. However, all data were obtained under conditions where the surface was covered by nearly a full layer of molecularly adsorbed CO. In a complete study, including XPS measurements of adsorbate coverage, Schwartz et al. determined the temperature effects on CO oxidation on Rh(111) [7]. They reported a maximum in the rate of CO oxidation at low pressures at $\approx$ 400–550 K, depending on CO/O_2 ratio. They found that the surface was dominated by CO at low temperatures and by oxygen atoms at high temperatures, as also reported by others [2,4,8]. Surprisingly, there have been no studies in which the rates of reaction on different single crystal planes have been compared directly.

We report molecular beam studies using Rh(110) and (111) planes and show that there are two regimes of temperature with different reaction characteristics; at low temperatures the reaction is indeed structure insensitive on rhodium, while at high temperatures it is strongly structure dependent. The molecular beam system used for this work has been described in detail elsewhere [9], but it can be described as a single collision reactor (SCR), which is ideal for the study of the kinetics of catalytic reactions which can be carried out at high conversion under UHV conditions. It delivers a beam of molecules of intensity typically 3×10^{13} molecules cm^{-2} s^{-1} (for a source pressure of 10 Torr CO) into a well defined spot on the surface 2.9 mm in diameter.

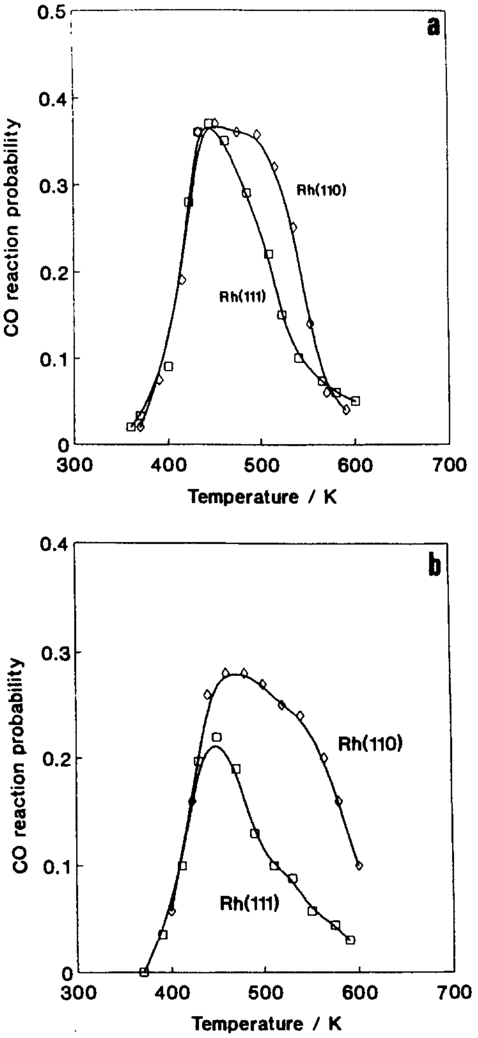

Fig. 1. Pseudo steady state measurements for Rh(110) (diamonds), and (111) (squares), as described in the text: (a) pressure ratio CO/O_2 2/1; (b) pressure ratio CO/O_2 4/1; (c) CO and oxygen coverages during reaction (a), estimated from data given in ref. [9].

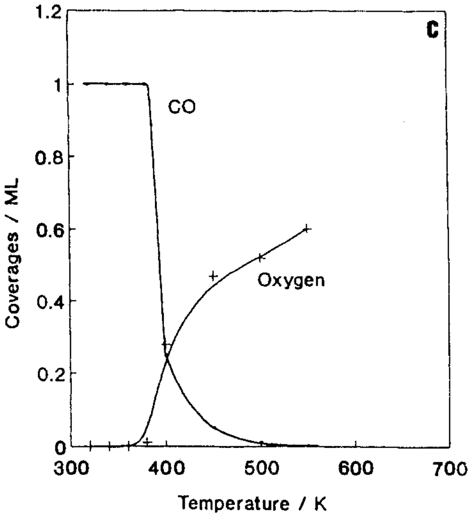

Fig. 1. Continued.

Fig. 1 shows experiments carried out using mixed beams of carbon monoxide and oxygen. Data are presented for Rh(110), a relatively open, high surface free energy plane, and Rh(111), the close-packed low energy surface. The experiments are pseudo steady state rate measurements in which the catalyst surface is initially exposed to the mixed beam at a low temperature at which the steady state production rate of CO_2 is very low, typically 370 K. After achieving steady state at 370 K, the temperature of the crystal is increased at 10 K min^{-1}, maintaining exposure to the mixed beam and observing the CO_2 production rate. As can be seen this reaches a maximum at ≈ 450 K and then declines, falling below our limit of detection at about 600 K. Fig. 1 also shows that the observed rates of CO oxidation are the same for Rh(110) and (111) at $T \lesssim 430$ K, but diverge markedly above this temperature. The ratio of the reaction rates on the two planes is shown in fig. 2, emphasising the structure dependence in the higher temperature regime. The reaction rate also becomes quite sensitive to the relative pressures of the CO and oxygen, and overall the data for Rh(111) look remarkably similar to those reported by Schwartz et al. [7] measured under similar conditions, but using background dosing and true steady state determinations.

To understand these differences we must establish the state of the catalyst surface in the different temperature regimes. As discussed elsewhere, the molecular beam apparatus permits precise instantaneous coverage determinations during reaction, since molecular impact rates, pumping speeds and mass spectrometer response factors have all been carefully determined [8,9]. Fig. 1c shows results from a series of steady state experiments [8] indicating how the surface coverages of oxygen and carbon monoxide change as the temperature is increased on Rh(110); similar results were observed on Rh(111) [10]. Carbon dioxide is only weakly

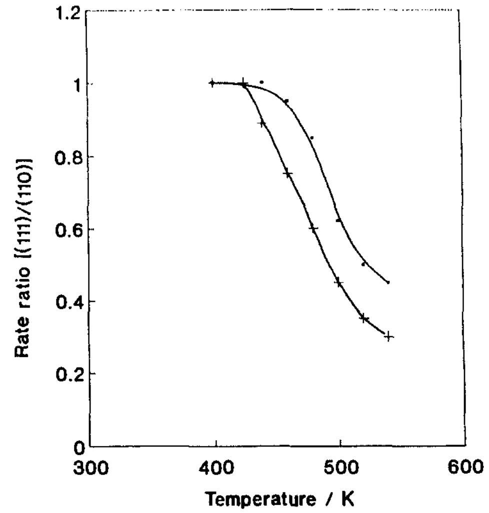

Fig. 2. Ratio of rates on the (110) and (111) planes determined from fig. 1, as a function of temperature; (squares) CO/O_2 pressure ratio 2/1; (crosses) CO/O_2 pressure ratio 4/1.

adsorbed on rhodium, so its coverage is very low throughout the experiments. At low temperatures, where the reaction is structure insensitive, the surface is saturated with CO, and the absolute coverage is very similar on Rh(110) and (111) at $9.8 \pm 0.5 \times 10^{14}$ molecules cm^{-2}. The rate limiting factor at these low temperatures appears to be the opening up of sites for oxygen adsorption, by CO desorption. The energetics of the CO adsorption at high coverage are similar on the two planes, as evidenced by the thermal desorption spectra shown in fig. 3, the desorption energy at high coverage is ≈ 130 kJ mol^{-1}. Oh et al. [5] have shown that the reaction activation energy in this regime is similar to the CO desorption energy. Thus

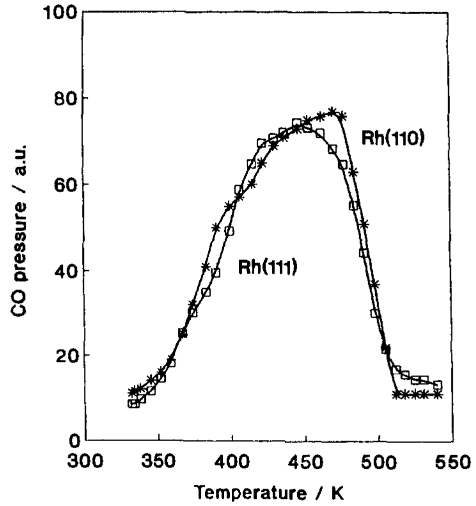

Fig. 3. CO desorption curves from Rh(111) (squares); and Rh(110) (stars).

the reason for structural independence in this temperature regime is the similarity in the desorption energy of CO between the two planes.

In contrast, in the structure sensitive regime at higher temperatures the surface is dominated by adsorbed oxygen. The oxygen coverage on both planes is similar and high, about half that of the chemisorbed monolayer, about $6.6 \pm 0.05 \times 10^{14}$ atoms cm^{-2}. Since the reaction occurs by a Langmuir–Hinshelwood interaction between CO_{ads} and O_{ads}, the significantly lower rate on Rh(111) must be the result of either a decreased CO coverage or an increased activation energy. Since the range of CO binding energies on Rh(111) is similar to that on (110) (see fig. 3), it is probable that the activation barrier to reaction is higher on Rh(111). This is supported by evidence that oxygen is, surprisingly, more strongly bound on the (111) surface than on Rh(110); the highest coverage desorption peak on (110) is at 800 K [11], whereas on (111) it is at 850 K [13]. There is also a multiplicity of oxygen desorption states on (110) associated with a series of surface reconstructions [11,12], whereas the desorption is apparently much simpler on Rh(111) [13]. If the oxygen is more strongly bound on Rh(111) than on (110), the activation barrier to surface reaction can be expected to be higher.

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References

[1] K.C. Taylor, *Catalysis*, Vol. 5, eds. J.R. Anderson and M. Boudart (Springer, Berlin, 1984) p. 119.
[2] C.T. Campbell, S.-K. Shi and J.M. White, Appl. Surf. Sci. 2 (1979) 382.
[3] C.T. Campbell, S.-K. Shi and J.M. White, J. Phys. Chem. 83 (1979) 2255.
[4] Y. Kim, S.-K. Shi and J.M. White, J. Catal. 61 (1980) 374.
[5] S.H. Oh, G.B. Fisher, J.E. Carpenter and D.W. Goodman, J. Catal. (1986) 360.
[6] C. Peden, D.W. Goodman, D.S. Blair, P.J. Berlowitz, G.B. Fisher and S.H. Oh, J. Phys. Chem. 92 (1988) 1563.
[7] S. Schwartz, L.D. Schmidt and G.B. Fisher, J. Phys. Chem. 90 (1986) 6194.
[8] M. Bowker, Q. Guo and R.W. Joyner, Surf. Sci. 280 (1993) 50.
[9] M. Bowker, P.D.A. Pudney and C.J. Barnes, J. Vac. Sci. Technol. A8 (1990) 816.
[10] M. Bowker, Q. Guo, Y. Li and R.W. Joyner, to be published.
[11] E. Schwarz, J. Lenz, H. Wohlgemuth and K. Christmann, Vacuum 41 (1990) 167.
[12] M. Bowker, Q. Guo and R.W. Joyner, Surf. Sci. 253 (1991) 33.
[13] T.W. Root, L.D. Schmidt and G.B. Fisher, Surf. Sci. 134 (1983) 30.