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## Molecular beam studies of CO oxidation and noxidation on Rh(110)

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**Abstract.** The reaction of CO with O<sub>2</sub> and NO on Rh(110) has been studied using a thermal molecular beam system. For both reactions the rate is low at high temperatures due to the formation of reconstructed, oxidized Rh.

Rh is an essential element in catalysts used for the control of pollution emitted from internal combustion engines. It is responsible for the activity of these catalysts for NO<sub>x</sub> conversion to nitrogen. Since legislation is tending to force car manufacturers to produce vehicles with lower and lower emissions as the years go by, it will be increasingly necessary to make more efficient use of the active components of the catalyst. With this in mind, it is most important to understand how these catalysts work at all levels, and the present work is aimed at increasing the knowledge of the basic mechanism and kinetics of the main reactions involved in CO, NO, H<sub>2</sub> and hydrocarbon conversion on well-defined Rh surfaces.

In this work, a thermal molecular beam system has been used to examine the adsorption of CO, O<sub>2</sub> and NO on Rh(110) and to study their reactions together. The beam system has been described in detail elsewhere [1]. In brief, it produces a beam of  $3 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-1</sup> intensity as a spot 2.9 mm in diameter at the crystal surface. The adsorption of CO, O<sub>2</sub> [2] and NO [3] is described elsewhere and can be summarized as follows. CO adsorbs molecularly with a high sticking coefficient,  $s$  (0.67) to give a monolayer coverage at 310 K, with a p(2×1) p1g1 arrangement on the surface. The shape of the decrease of  $s$  with coverage indicates precursor type kinetics for adsorption. It desorbs in the range 370–500 K, showing repulsive lateral interactions which shift the main peak and produce low temperature shoulders. Oxygen adsorbs dissociatively ( $S_O = 0.62$ ) and saturates at around 0.7 monolayer of atoms; it desorbs at ~ 1100 K at low coverages and broadens to lower temperature as the coverage increases, at saturation desorption begins at ~ 800 K. It is most important to note that oxygen grossly reconstructs the Rh surface, forming a complicated series of structures in LEED. NO adsorbs initially dissociatively, with a similar sticking coefficient to CO, but after saturation of the atomic states molecular NO is stabilized. Desorption yields NO at 390 K, N<sub>2</sub> at 410 K and O<sub>2</sub> above 750 K. NO dissociates to give total coverages of atoms (N+O) of ~ 1.4 monolayers, if adsorption is carried out at 400 K.

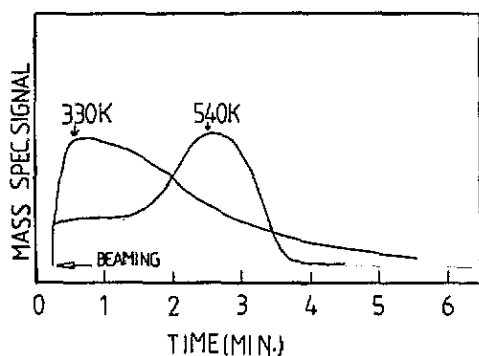


Figure 1.  $\text{CO}_2$  evolution curves at 330 K and 540 K for CO in the molecular beam reacting with 0.65 monolayers of oxygen predeposited on the surface.

The reaction of CO and  $\text{O}_2$  can be summarized as follows, and examples of transient reactions are shown in figure 1; a full layer of CO preadsorbed blocks oxygen dissociation completely at 330 K, whereas the opposite is not the case (figure 1). Reaction of CO with a full layer of oxygen atoms is fast, yielding  $\text{CO}_2$  into the gas phase. However, some CO and oxygen remain on the surface after the experiment shown in figure 1 and can be desorbed (the oxygen reacting with CO to give  $\text{CO}_2$ ) by heating. This is due to the fact that, as the oxygen is removed, its binding to the surface increases (higher desorption temperature [2,4]) and the surface reaction activation barrier also goes up. Kinetic modelling of the reaction indicates a variation from  $56 \text{ kJ mol}^{-1}$  for high oxygen coverages to around  $80 \text{ kJ mol}^{-1}$  for low oxygen coverages. Although the 330 K  $\text{CO}_2$  evolution shown in figure 1 looks simple, modelling is nevertheless difficult, involving the necessity of including CO and oxygen coverage dependence of the reaction activation energy; the detailed kinetic modelling will be published elsewhere [5]. The reaction becomes much more complex at elevated temperatures, as evidenced by the 540 K  $\text{CO}_2$  evolution curve, which shows a very slow initial rate of CO oxidation. LEED indicates that this low rate is associated with the high coverage restructured surface [c(2×6) and p(2×3) p1g1] and that the increase in rate is associated with transformation to the lower coverage p(2×2) glide-line structure. The major difference between these structures is that the higher coverage one was proposed to be due to a denser Rh surface [more (111)-like] than the 0.5 monolayer (p(2×2)) structure, which although restructured, contains the same number of Rh atoms as in the original (110) surface [2]. It was proposed that the c(2×6) may consist of a subsurface layer of oxygen.

The low reactivity seen upon introducing CO to the oxygen patch gets lower the higher the temperature at which the reaction is carried out. It is likely that this is due to reaction taking place at a limited number of sites on the surface and that the lifetime and mobility of a CO precursor state (perhaps physisorbed) determines how fast the reaction takes place on the restructured surface. At high temperatures the lifetime is short and therefore few sites are visited during the sojourn of the CO on the surface, hence, there is a low reaction probability.

The reaction of CO and NO shows similar features to CO oxidation. Thus, at 310 K, the CO<sub>2</sub> evolution is similar to that in figure 1 if a half monolayer of NO is pre-deposited. However, a full layer of NO blocks CO adsorption very effectively, whereas NO can react (albeit slowly) with a full layer of CO. This enhanced competition of NO for sites is reflected in steady state measurements with a mixed beam, which show a lower rate of CO<sub>2</sub> production over most of the temperature range. A more detailed report of this work on the CO/NO reaction will be submitted shortly.

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