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Shedding light on catalytic ignition: coverage changes during CO oxidation on Pd(110)

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Catalytic ignition or ‘light-off’ has been studied for a reaction of importance in automobile exhaust emissions, namely, CO oxidation over Pd, a metal which has become an important component of car catalysts. We present kinetic and spectroscopic studies to show that light-off is associated with a step change in surface composition of reactants as the surface is heated. Fast XPS using synchrotron radiation of high brightness reveals that the surface is dominated by CO at low temperature and the coverage suddenly switches during light-off to an oxygen-atom-dominated situation.

Keywords: carbon monoxide, light-off, molecular beam, oxygen, Pd(110), synchrotron radiation, XPS

Light-off of a reaction is important both industrially and academically. Industrially, many catalysed reactions, especially those involving oxidation, show a self-acceleration in which the rate of reaction can rapidly change from a low level to a high level. This is known as light-off, and such systems are said to show bistability. In some cases, this can make reactions difficult to control and occasionally it can have disastrous consequences. In the case of automobile exhaust gas catalysis, light-off is very important, because below the critical temperature at which this occurs the catalyst inefficiently removes pollutants (such as hydrocarbons, NO_x and CO) whereas above this temperature the catalyst works very efficiently. There is a current drive to reduce light-off temperatures in car catalysts in order to decrease the time between engine turn-on and the efficient conversion of the exhaust pollutants. Academically, light-off is associated with the field of catalytic oscillations which is one of the most studied areas of current scientific endeavour in surface reactions, but is more generally related to ignition. Since light-off is a result of a self-accelerating reaction, when combined with a feedback mechanism it forms an integral part of any sustained oscillation scheme; it is associated with the rising edge of a cycle of oscillating reaction rate [1,2].

There has been much discussion in the literature regarding the fundamental cause of the step change in reactivity during light-off [3–7]. The nature of the catalyst surface before, after, and most importantly, during light-off has not been reported to our knowledge. In this paper we present direct spectroscopic evidence for the concentration of reactant species on the surface, showing that there is a non-linear step change in surface composition at light-off. We have combined both kinetic and spectroscopic measurements to probe the light-off reaction in a low pressure environment on a Pd(110) single crystal. The kinetics were measured using a molecular beam catalytic reactor which is operated in a pseudo-steady-state mode. This reactor generates a directed beam of thermal gas molecules (in our experiments a mixture of CO and O_2) which impinge on the surface with an in-beam pressure of approximately 1.6×10^{-7} mbar. A quadrupole mass spectrometer measures the reflected gas and desorption products. The details of this methodology are given elsewhere [8]. The identification of surface species was achieved by employing X-ray photoelectron spectroscopy (XPS) in which a synchrotron X-ray source was used, namely, Elettra at Sincrotrone Trieste, Italy. The particular utility of this machine is its high brightness in the soft X-ray region, its tuneability to optimise ionisation cross-sections and that the photoemission intensity is proportional to surface composition, i.e., an absolute measurement of surface species. In fact, the data acquisition time for taking XPS spectra at the SuperESCA beamline can be cut by about three orders of magnitude compared with a conventional laboratory source. Individual spectra can be obtained on the time scale of several seconds, and surface reactions can be directly followed in a reasonable time period.

Figure 1 shows data for the reaction between CO and O_2 (in a $1:1$ ratio) to form CO_2, in terms of the CO_2 partial pressure detected at the mass spectrometer as a function of both time and temperature as the sample is heated stepwise in the presence of the beam of molecules. The CO and O_2 mixture is introduced onto the sample maintained at 315 K (at time ∼100 s), and a peak in CO_2 production is observed at point A. This is due to adsorption and build-up of CO and O_2 on the surface and subsequent reaction. However, the rate then diminishes to an immeasurably low level (point B), essentially zero CO_2 production. As the sur-

Figure 1. Production of CO_2 and stepwise change in temperature for a mixed dose of CO and O_2 onto clean Pd(110) with respect to time. The dose is started just prior to point A, where a transient reaction to produce CO_2 occurs, which rapidly ceases. From point B, the temperature is increased in a stepwise manner. Point C is the light-off and results in a sharp reaction rate maximum. At point D and for all higher temperatures, the reaction rate decreases.

face is heated, no net adsorption or reaction appears to take place until around 360 K when there is a rapid increase in reaction rate which goes through a sharp maximum, light-off (point C). This high rate is not sustained and drops to a lower steady-state level (point D), thereafter incremental steps in temperature result in decreased reaction rate. The overall shape of this curve above the light-off temperature has been seen before, for instance, by Ladas et al. [9], that is, low rates at high and low temperature, with a single rate maximum at intermediate temperatures. The description of this behaviour has been given in terms of adsorbate coverages, with CO dominating the surface at low temperatures, atomic O dominating at high temperature. The nature of the thermodynamics of adsorption largely dictates these gross effects. The heat of adsorption of CO (ca. 100–140 $\mathrm{kJ\,mol^{-1}}$ [10]) results in high coverage at low temperatures, and low coverage at high temperatures; oxygen will dominate in the latter regime due to its higher heat of adsorption.

Figure 2 presents the XPS data which give direct information on the detailed relationship between this light-off and adsorbate coverage. The left panel shows the C(1s) region of the XPS spectrum while the O(1s) from a similar experiment is shown in the right panel, from which the $3p_{3/2}$ contribution from Pd at a binding energy of 533 eV has been subtracted. The O(1s) region shows signal characteristic of atomic O and molecular CO at binding energies of 530.3 and 532.2 eV, respectively, while the C(1s) is solely due to CO (CO_2 desorbs immediately upon produc-

Figure 2. C(1s) and O(1s) spectra of Pd(110) for a mixed CO and O_2 dosing experiment as described in figure 1. The side panels show photoemission intensity from individual spectra that are rapidly acquired as a function of time, where blue is the most intense emission and black is the lowest. The surface temperature is increased stepwise in a similar manner to figure 1. The centre panel displays individual spectra of the O(1s) spectrum at key-points in the reaction. The surface temperature and elapsed time are indicated for each spectrum. Spectra A–D correspond to the points indicated in figure 1. The O(1s) signals from $CO_{(a)}$ and $O_{(a)}$ are seen at 532.4 and 530.4 eV, respectively. The spectra at light-off, point C, show a sudden change in surface coverage from CO- to O-dominated.

Figure 3. Coverages of $CO_{(a)}$ (red) and $O_{(a)}$ (blue) as well as their sum (green) versus time from figure 2. The black curve represents the temperature. The coverages have been calculated by integrating the spectra over the binding energy region 534.4–531.2 eV ($CO_{(a)}$), respectively 531.2–528.9 eV ($O_{(a)}$), using the background subtracted spectra, and by comparison to reference spectra of c(2×4)-O (0.5 ML), respectively (2×1)-CO (1 ML). At high $O_{(a)}$ coverages the $CO_{(a)}$ signal has been corrected for a background contribution due to the high binding energy tail of the $O_{(a)}$ signal.

tion). The left and right panels of this figure are composed of multiple spectra, a selection of which are shown in the centre panel at critical stages in the reaction. The coverages of the CO and the O species as well as their sum are displayed in figure 3, as calculated by integration over the respective XPS peaks and comparison to reference spectra for CO and oxygen adsorbed alone. In figures 2 and 3 the temperature is increased in a stepwise manner.

As the 1 : 1 mix of CO and O_2 is introduced at 300 K onto the clean surface, the O signal at 530.3 eV initially rises (point A), but then is rapidly lost by reaction from the surface at this low temperature while CO continues to adsorb. The surface then appears free of oxygen atoms and is saturated in CO (point B). A stepwise increase of the temperature reduces the CO coverage – first very rapidly, around a temperature of 320 K, a decrease which can be attributed to a transition from a (2×1)-CO to (4×2)-CO superstructure, the latter with a saturation coverage of around 0.75 ML [11,12]. This transition leads to the shift of the CO O(1s) binding energy from 532.8 to 532.2 eV. Thereafter the CO coverage is further reduced due to an increasingly significant desorption rate, and is replaced by a small coverage of O. As shown in figure 3, the overall coverage (green curve) remains approximately constant during this replacement. At 387 K the CO signal diminishes rapidly but not to zero, and the O signal rises in a similar manner. This point corresponds to light-off, point C in the molecular beam data. Further stepwise increments in temperature result in a continued reduction in the already small CO coverage (point D).

As can be seen, the total coverage is almost constant during and after light-off. The oxygen coverage built up just after the light-off is around 0.4 ML, lower than the 0.5 ML saturation coverage of oxygen at temperatures above 400 K [13]. This coverage is associated with a c(2×4) superstructure, which involves a (1×2) substrate reconstruction as does the (4×2)-CO superstructure. This leads us to the conclusion that the light-off process as observed here is not due to a change in long range substrate reconstruction.

The autocatalytic nature of the abrupt change in surface reactivity cannot be rationalised on a heat production basis since the reaction is isothermal at the low pressures used in the experiment. One possible explanation for the light-off can be an autocatalytic increase of vacant sites by the two reaction steps of dissociative oxygen adsorption and reaction of the adsorbates in the presence of a CO adsorption/desorption equilibrium. This can be described as follows:

$$2CO_{(a)} + O_{2(g)} + 2* \rightarrow 2CO_{2(g)} + 4*$$

where the asterisks denote free adsorption sites. The starting point for the light-off is a CO-covered surface, where the dissociative oxygen adsorption is considerably inhibited. It is important to note here that CO adsorption requires one free site per molecule while dissociative oxygen adsorption requires two. Thus when the number of free sites is low, oxygen adsorption is inhibited; the number of free adsorption sites is rate limiting. As soon as the CO coverage drops by desorption or reaction below a certain inhibition coverage, the reaction becomes strongly accelerated by autocatalysis, the light-off takes place.

This vacant site autocatalysis has already been discussed and simulated extensively for a lot of reaction systems under low pressure conditions (see, e.g., [14]). Simulations are based in this case on the assumption that there is a critical coverage of a dissociation inhibiting molecule, above which a rate limiting dissociation step is completely poisoned. This means that the surface before light-off is just described by an adsorption/desorption equilibrium of the inhibiting species; the surface is covered only by the inhibitor.

However, a closer look with fast XPS reveals, at least for this reaction system, that the situation is not that simple: there is already a considerable oxygen coverage on the surface before light-off amounting to about one-fourth of the saturation value. This oxygen is indeed reactive, as can be seen in figure 1, where the reaction rate has already begun to rise before the light-off (i.e., before point C); the coverages of the reacting species are steady-state coverages on a moderately reactive surface. This experimental finding corresponds to simulation results of Vlachos et al. for the $H_2 + O_2$/Pt(foil) system at high pressures, where the catalytic ignition is controlled by the hydrogen pressure: before a homogeneous ignition takes place at higher temperatures, the surface is found to be covered partially by oxygen [7].

Although the reaction is already taking place at a moderate rate, the oxygen coverage available at this point is not able to light the reaction. We deduce therefore from

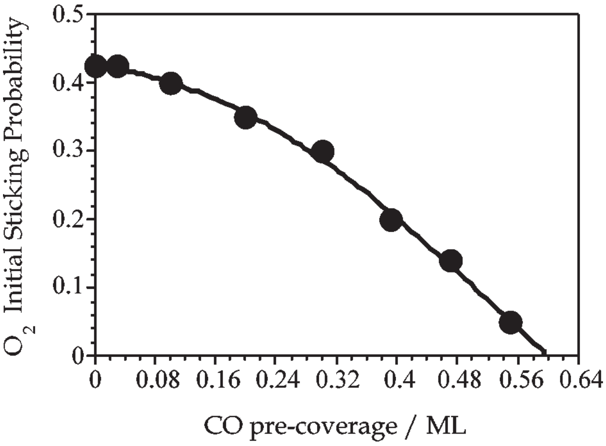

Figure 4. The initial sticking probability of O_2 on Pd(110) which has been pre-dosed with different CO coverages. Experimental error is represented by the size of the points. The results show that oxygen sticking is blocked at a CO pre-coverage of around 0.6 ML.

the XPS data that it is necessary to make a distinction between an inhibition coverage for the dissociative oxygen adsorption (and the following reaction) and an inhibition coverage for the autocatalytic propagation of the reaction, which do not coincide. To clarify this, we have carried out measurements with the molecular beam in which different coverages of CO were adsorbed on the surface first before determining the O_2 sticking probability. The results are shown in figure 4 and confirm total inhibition of O_2 dissociation at a CO coverage of around 0.6 (±0.06) monolayer. This is a similar blocking coverage to that found for Rh(110) for which the critical coverage was found to be 0.75 (±0.08) [15]. Since the total coverage remains constant in the region before light-off, the inhibition coverage for the autocatalytic propagation has to depend on the partial CO coverage. Only if the partial coverage of CO drops to around 0.4 ML does the autocatalytic reaction take place. On the other hand, the dissociative oxygen adsorption and reaction can already take place if the CO coverage drops slightly below 0.6 ML.

During the light-off, the CO_2 production rate shows a strong sharp peak which decays to a background level, as would be expected of an autocatalytic mechanism which breaks down once the inhibiting coverage has been reacted off. The system is switched to the high reaction rate branch, which is characterised by a high oxygen coverage which is not inhibiting the CO adsorption. The reaction rate then decreases with increasing temperature in the region between points C and D due to the reduction in the low equilibrium concentration of $CO_{(a)}$ on the surface, mainly due to an increased desorption rate.

In conclusion, we have shown, by direct spectroscopic methods, that the light-off phenomenon is associated with a switch of surface coverages between a dominant coverage of one adsorbate and another. The low rate reaction branch is associated with a CO-dominated and poisoned surface on which O_2 dissociation is strongly inhibited, the high rate branch is associated with an oxygen-dominated surface which does not poison CO adsorption. This behaviour is likely to be general for CO oxidation on metals, as long as no surface reconstructions are involved.

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