In situ FTIR-microspectrometry: Spatial Differentiation of CO During Chemisorption and Oxidation on highly orientated Graphite-supported Pt

Valerie A. Self and Paul A. Sermon
Department of Chemistry, Brunel University, Uxbridge, Middx UB8 3PH, UK

FTIR-microscopy has been used *in situ* to characterise catalyst surfaces; with CO on graphite-supported Pt during chemisorption and oxidation it reveals surface heterogeneity and may suggest that the more reactive bridge-bound CO is predominantly found at the outer edge of CO islands on the surface.

FTIR has been extensively used for the detection of adsorbates on catalyst surfaces,[1] but now FTIR-microspectrometry has become available using FTIR analysis of surfaces resolved in an infra-red microscope. To test its potential, the method has been used to probe the nature of adsorbed CO.[2]

Owing to its high degree of perfection at an atomic level, highly orientated pyrolytic graphite (HOPG) has been used as a standard for scanning tunnelling microscopy.[3] Here it has been coated with Pt by vacuum deposition to form a sample of polycrystalline Pt/C which is well defined. Specifically the HOPG sample was sputter-coated with Pt for 30 min. This sample was placed in the FTIR cell within the IRPLAN (Spectra-Tech) IR microscope linked to a Perkin Elmer 1710 FTIR, through which the reactant gases could flow as follows: (i) in chemisorption 6% CO/N_2 flowed at 23 ml min^{-1} while heating to 425 K at 5 K min^{-1} and holding at 425 K for 45 min, (ii) in CO oxidation where 6% CO/N_2 (21.4 ml min^{-1}) and 6% O_2/N_2 (21.1 ml min^{-1}) flowed while heating to 425 K at 5 K

min^{-1} and holding isothermally for 2 h before cooling to room temperature. It was then possible to measure reflectance FTIR spectra for selected areas of the surface of the catalyst using 50 scans with no subsequent smoothing and with a resolution of 8 cm^{-1}. Reflectance spectra for the Pt/HOPG catalyst in CO chemisorption and CO oxidation are shown in Figure 1.

In CO chemisorption and oxidation it is possible to differentiate linearly-bound and bridge-bound CO by IR.[4]

Consistent with analysis of CO on low index crystallographic planes of Pt[5] the following assignments are made: (i) the peak at 1890 ± 9 cm^{-1} is bridge-bound CO, (ii) weaker bands at 1933, 1953, and 1982 ± 2—4 cm^{-1} (γ), and (iii) the peak at 2082 ± 1 cm^{-1} is linearly-bound CO.

From Figure 1 for CO chemisorption it is clear that the ratio of bridge : linear CO and the extent of observation of smaller bands at 1899 and 1982 cm^{-1} varies with analytical position. In other words the surface is not entirely homogeneous with
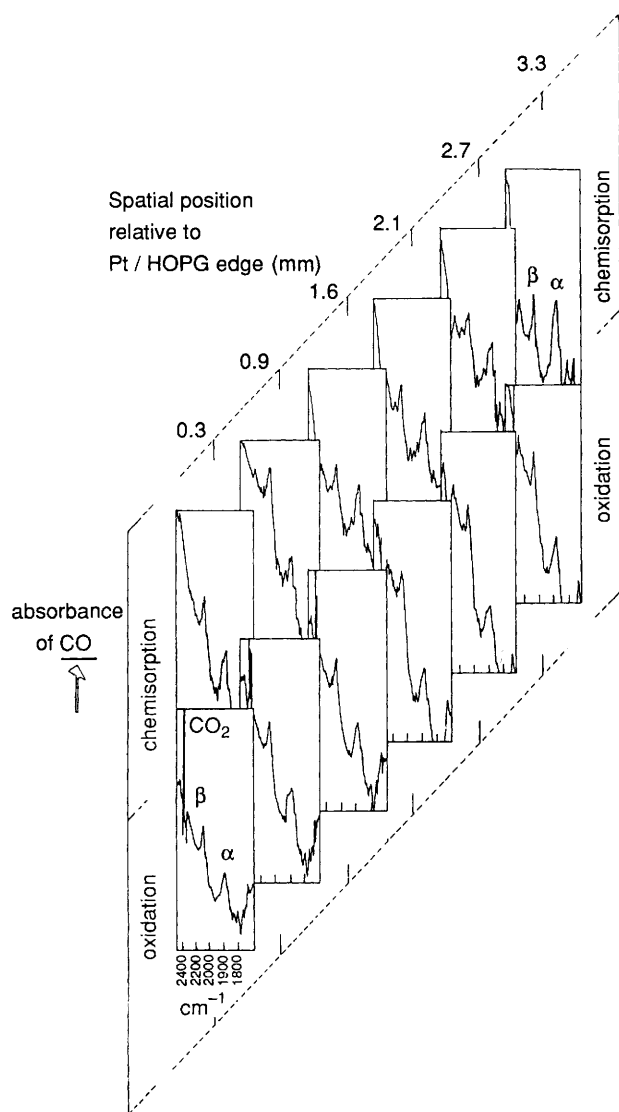
Figure 1. Reflectance FTIR-microspectroscopy during chemisorption and oxidation on Pt/HOPG at different positions across the surface of the single crystal. The α and β peaks denote bridge- and linearly-bound CO. The optical resolution of the microscope was 4.4 μm.
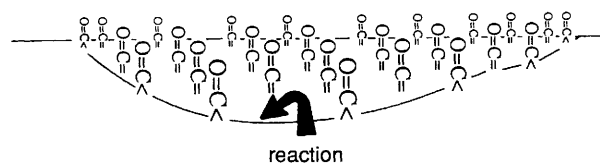

Figure 2. Reaction at the perimeter of a CO island on a Pt surface.

Although since the mid 1950s infra-red has been used to identify adsorbed species on the surfaces of solids and catalysts, it often remains uncertain whether the species detected are the important participants in surface reactions rather than mere spectators (which may numerically exceed the more reactive metastable short-lived participants).

Hence the present *micro*spectroscopy may be useful in understanding the microchemistry of catalytic surfaces. Here in CO oxidation it suggests that the surface is not uniformly reactive (and this is consistent with the presence of reactant islands). Ultimately, this may allow us to understand and control activity-selectivity of such surfaces *via* fractality-diffusional modes. This new analytical approach could lead to heterogeneous reactions being more effectively and selectively catalysed by surfaces which are well understood and properly optimised.

It may be that the present approach also provides a method of relating surface chemistry of catalysts to surface science and practical catalysis.

If CO islands exist on the surface then the local θ_{CO} will be high at their centres (where linearly-bound CO will dominate) and low at the edges (where bridge-bound CO is likely to dominate). Therefore it is not surprising that it is at these edges that reaction occurs involving bridge-bound CO, as illustrated in Figure 2.

The present findings with regard to chemical heterogeneity at the catalyst surface are important and support the postulate of Hinshelwood some fifty-five years ago.

respect to CO adsorbate. In CO oxidation CO_2 is observed (at 2360 cm^{-1}) when the smaller γ peaks are not observed, suggesting that these smaller γ peaks are associated with the most active species in CO oxidation on this Pt. In addition, the peak for bridge-bound CO is shifted to 1887 ± 1 cm^{-1} (while the linearly held CO peak remains at about its earlier level in CO chemisorption) and decreases in intensity. Therefore linearly bound CO may be most unreactive on this surface and unaffected by the presence of O, unlike the more reactive bridge-bound CO.

The surface diffusion coefficient for oxygen is smaller on Pt[6] than that for CO, although both may be decreased substantially as the surface becomes less energetically homogeneous,[6,7] and this may then be the cause of the spatial differences of CO on the Pt/HOPG seen here in adsorption and the segregation of reactants in catalysis.[8,9]

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