IN SITU ANALYSIS OF CO DURING CHEMISORPTION AND OXIDATION ON GRAPHITE-SUPPORTED Pt BY FTIR-MICROSPECTROMETRY

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SUMMARY

For chemisorption and oxidation on Pt/HOPG (highly-orientated pyrolytic) graphite, reflectance Fourier Transform Infrared (FTIR)-microspectrometry reveals a variable state and reactivity for CO.

INTRODUCTION

Even for model surface science systems, where surface heterogeneity (ref. 1) is minimal, surface diffusion may be too slow relative to the reaction rate to avoid segregation of reactants into surface islands (ref. 2) under steady-state conditions. Thus in CO oxidation on Pt (where the relevant surface diffusion coefficients are such that $D_O < D_{CO}$ (ref. 3)) then reactant CO islands exists (refs. 4,5) at the perimeters of which the surface reaction is thought to occur (ref. 6). Furthermore CO can chemisorb on metals in linear (atop) and bridge forms to extents which vary with the precise faces predominantly exposed (ref. 7), coverage, etc.

Infrared has long been used to probe the nature of adsorbed CO (ref. 8) on model film and heterogeneous surfaces, but it may now be that FTIR-microspectrometry will allow the state of this adsorbate and reactant to be investigated with a spatial resolution of 4.4 μm on model (and real) catalytic surfaces.

EXPERIMENTAL

Because of its high degree of perfection at an atomic level, highly orientated pyrolytic graphite (HOPG) has been used as a standard for scanning tunnelling microscopy (ref. 9). 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 to give a Pt layer 60 nm in thickness. No other metallic impurities were detected.

The sample was placed in the FTIR cell within the IRPLAN (Spectra-Physics) 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 while heating to 425K at 5K/min and holding at 425K for 45 min before cooling to room temperature;

(ii) in CO oxidation where 6% CO/N_2 (21.4 ml/min) and 6% O_2/N_2 (21.1 ml/min) flowed while heating to 425K at 5K/min and holding isothermally for 2h before cooling to room temperature.

Using this IR microscope it was possible to measure reflectance FTIR spectra for selected areas of the surface of the catalyst. All spectra were measured using 50 scans with no subsequent smoothing and with a resolution of 8 cm^{-1}.

In CO chemisorption and oxidation it is thus possible to differentiate linearly-bound and bridge-bound CO by IR (ref. 10).

RESULTS

Reflectance spectra for the <u>surface</u> CO and CO_2 species on Pt/HOPG catalyst in CO chemisorption and CO oxidation are shown in Figure 1, where the area being sampled is 440 μm^2. No significant gas phase bands were noted in this region.

Consistent with analysis of CO on low index crystallographic planes of Pt (ref. 11) the

(i) α peak at 1890 ± 9 cm^{-1} is bridge-bound CO;

(ii)   weaker bands at 1933, 1953 and 1982 ± 2.4 cm^{-1} are γ bands;

(iii) β peak at 2082 ± 1 cm^{-1} is linearly-bound CO.

In CO chemisorption it is clear that the ratio of $\alpha:\beta$ peaks varies with analytical position across the Pt/HOPG crystal; so does the extent of observation of γ bands. In other words the surface is not entirely homogeneous with respect to CO adsorbate. The intensity of the bridge-bound CO band is greater than was expected on Pt. In CO oxidation CO_2 is observed at 2360 cm^{-1} when the smaller γ peaks are not observed and the α peak is severely reduced relative to the intensity observed in chemisorption of CO alone. This suggests that the α and γ peaks are associated with the most active species in CO oxidation on this Pt, either because they are at the edge of <u>CO</u> islands <u>or</u> because their vibrational characteristics make the transformation <u>CO₂</u> easier. In addition, the α peak is shifted to 1887 ± 1 cm^{-1} while the β peak remains at about its earlier position in CO chemisorption: therefore linearly-bound CO may be quite unreactive on this surface and unaffected by the presence of <u>O</u>. On Pt/HOPG the apparently more reactive bridge-bound state <u>decreased</u> in intensity on CO oxidation, but the evidence of CO_2 formation and α/γ peak decrease is not uniformly exhibited by the whole surface.

DISCUSSION

The surface diffusion coefficient D_0 of oxygen is thought to be smaller on Pt (ref. 4) than that for CO, although both coefficients may be decreased substantially as the surface becomes less energetically homogeneous since the periodic nature of the potential energy surface governs (ref. 12) the whole question of surface mobility (ref. 4). This may then be the cause of the spatial difference of <u>CO</u> on the Pt/HOPG seen here in adsorption and catalysis. It may be that reactant islands are

important in defining catalysis since the perimeters of these might have highest densities of bridge-bound CO, but alternatively bridge-bound CO may from a vibrational point be more readily converted to CO_2. Nevertheless, the relationship of these results to those obtained* for Pt foil in CO oxidation, where active surface grains were seen, may be interesting.

Although since the mid 1950's infrared 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 which are responsible for catalysis.

The present microspectroscopy may be useful in understanding the microchemistry of catalytic surfaces in the sense that here in CO oxidation it suggests that the surface is not uniformly reactive (which 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 even better understood and properly optimised.

CONCLUSIONS

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

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CO chemisorption

adsorbance

CO_2

β peak

α peak
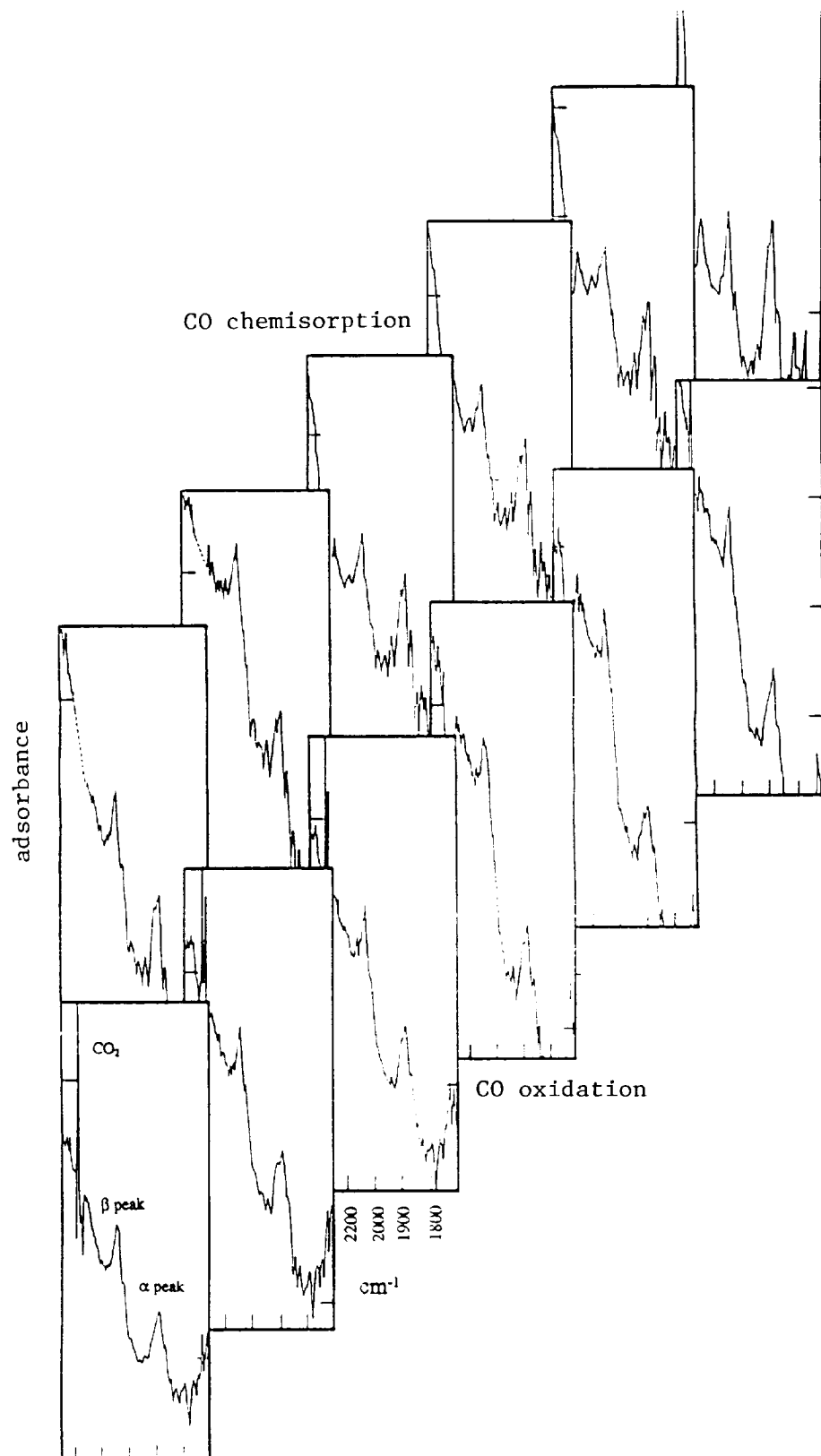
CO oxidation

2200 2000 1900 1800

cm^{-1}

Figure 1. Reflectance FTIR-microspectrometry during CO chemisorbed an oxidation on PT/HOPG.