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1989 J. Phys.: Condens. Matter 1 SB221

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***In situ* analysis of CO during chemisorption and oxidation on graphite-supported Pt by Fourier transform infrared microspectrometry**

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Received 12 May 1989

Abstract. For chemisorption and oxidation on Pt/highly oriented pyrolytic graphite, reflectance Fourier transform infrared microspectrometry reveals a variable state and reactivity for CO.

1. Introduction

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

Infra-red techniques have long been used to probe the nature of adsorbed CO [8] on model film and heterogeneous surfaces, but it may now be that Fourier transform infrared (FTIR)-microspectrometry will allow the state of this adsorbate and reactant to be investigated with a spatial resolution of $4.4 \mu\text{m}$ on model (and real) catalytic surfaces.

2. Experimental details

Because of its high degree of perfection at an atomic level, highly oriented pyrolytic graphite (HOPG) has been used as a standard for scanning tunnelling microscopy [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 spectrometer, through which the reactant gases could flow as follows.

(i) In chemisorption, 6% CO–N₂ flowed at 23 ml min^{-1} while heating to 425 K at 5 K min^{-1} and holding at 425 K for 45 min before cooling to room temperature.

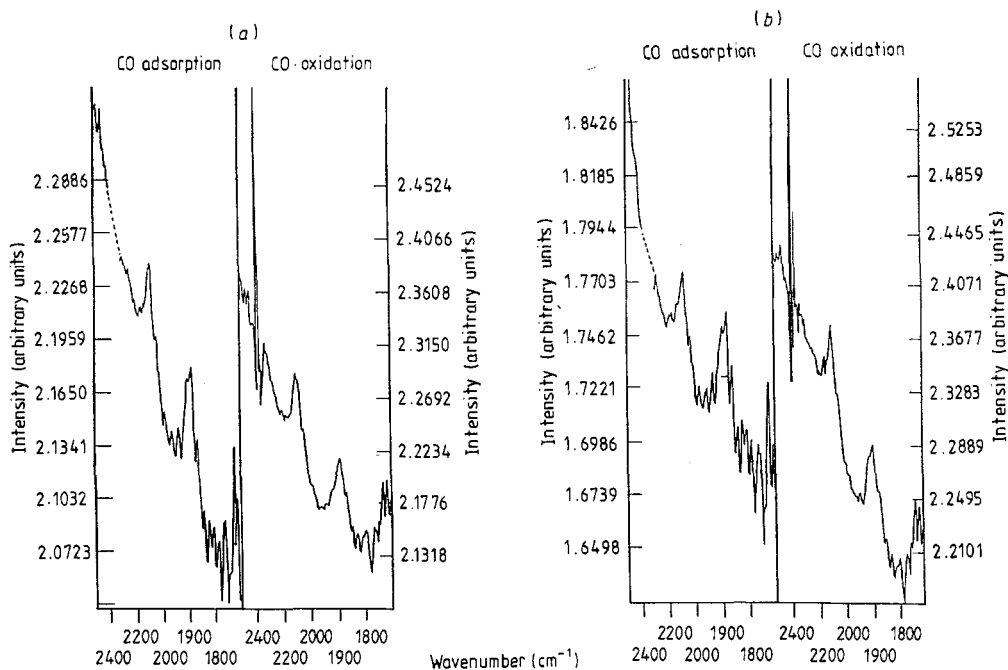


Figure 1. FTIR spectra (a) from the edge of Pt/HOPG and (b) from the centre of Pt/HOPG.

(ii) In CO oxidation, 6%CO-N₂ (21.4 ml min⁻¹) and 6%O₂-N₂ (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.

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 between linearly bound and bridge-bound CO by IR [10].

3. Results

Reflectance spectra for the *surface* CO and CO₂ species on Pt/HOPG catalyst in CO chemisorption and CO oxidation are shown in figure 1, where the area being sampled is 440 μm². No significant gas phase bands were noted in this region.

Consistent with the analysis of CO on low-index crystallographic planes of Pt [11] are the following.

- (i) The α -peak at 1890 ± 9 cm⁻¹ is bridge-bound CO.
- (ii) The weaker bands at $1933 \pm (2-4)$, $1953 \pm (2-4)$ and $1982 \pm (2-4)$ cm⁻¹ are γ -bands.
- (iii) The β -peak at 2082 ± 1 cm⁻¹ is linearly bound CO.

In CO chemisorption it is clear that the ratio of α - to β -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, CO₂ 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 the chemisorption of CO along, suggesting 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 CO islands or because their vibrational characteristics make the transformation to CO₂ 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 O. On Pt/HOPG the apparently more reactive bridge-bound state *decreased* in intensity on CO oxidation, but the evidence of CO₂ formation and α - and γ -peak decrease is not uniformly exhibited by the whole surface.

4. Discussion

The surface diffusion coefficient D_O of oxygen is thought to be smaller on Pt [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 [12] the whole question of surface mobility [4]. This may then be the cause of the spatial difference of CO 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 CO₂. Nevertheless, the relationship of these results to those obtained [13] for Pt foil in CO oxidation, where active surface grains were seen, may be interesting.

Although since the mid-1950s infrared techniques have 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 the more effective and selective catalyses of heterogeneous reactions by surfaces which are even better understood and properly optimised.

5. 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.

Acknowledgments

The support of VAS by SERC is gratefully acknowledged.

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