

Evidence for the Involvement of Weak Chemisorption in CO Oxidation on SnO_x-Supported Pt

Paul A. Sermon,* Valerie A. Self and Edward P. S. Barrett

Department of Chemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK

At 2168 cm⁻¹ FTIR spectroscopy reveals one notable difference in the states of CO adsorbed on silica- and SnO_x-supported Pt during chemisorption and catalysis; such a band is seen for Pt/SnO_x but not for Pt/SiO₂, this may correspond to weakly chemisorbed CO and because it exists only on the surface (Pt/SnO_x) of high activity in CO oxidation, the presence of such species may be consistent with higher rates of this surface reaction on Pt/SnO_x.

Dowden remarked¹ that 'weakly chemisorbed species are ubiquitous' and 'could reduce catalytic activation energies, change sticking coefficients and indeed bypass strongly held adsorbate species.' However, proof that weakly chemisorbed species are participant, rather than spectator, species in heterogeneous catalysis has not generally been forthcoming.

Here consideration is given to CO oxidation on (i) Pt/silica: for which the reaction should occur predominantly on the group VIII metal surface alone and the CO may be in both linearly and bridge-bound states,² and (ii) Pt/SnO_x: for which previous studies³ have shown that spillover enhanced CO oxidation activity. Catalysts involving group VIII metals and SnO_x are now being proposed for use in the re-oxidation of CO produced by decomposition in CO₂ lasers.⁴

EuroPt-1 Pt/SiO₂ has been described.⁵ 3%Pt/SnO_x was prepared by impregnation of the support (BDH; stannic oxide; 18 m² g⁻¹) with H₂PtCl₆ (Johnson Matthey); after equilibration for 24 h at room temperature, the catalyst was dried at 393 K for 18 h and then calcined at 773 K for 6 h. Both catalysts were characterised by photoelectron spectroscopy and hydrogen chemisorption. The Pt 4f(7/2) binding energy for Pt/SiO₂ was 71.4 eV and for Pt/SnO_x 75 eV and while Pt/SiO₂ chemisorbed 168–188 μmol H₂ g⁻¹_{cat}, Pt/SnO_x adsorbed only 14.2 μmol g⁻¹_{cat}. Both results imply a metal support interaction in Pt/SnO_x that involves some Pt^{x+} at the metal-oxide interface.

For the CO oxidation reaction 0.06–0.01 g catalysts were studied at 421–424 K in a microflow reactor. The reactive

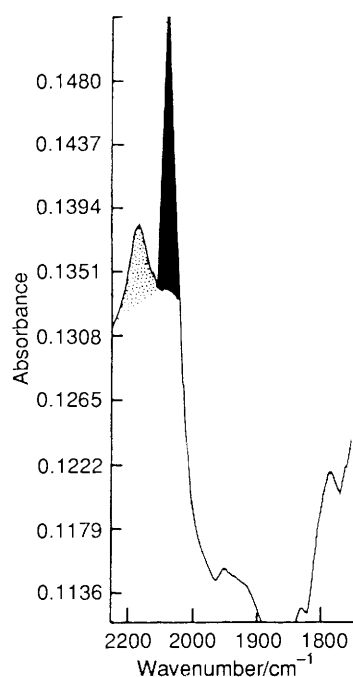


Fig. 1 Reflectance FTIR for weakly held (hatched) and linearly bonded (black) surface-CO species during CO chemisorption on Pt/SnO_x as measured in different segments of its surface; during catalysis of CO oxidation the hatched bands were depressed. Spectra were measured at 298 K after CO chemisorption or catalysis at 423 K.

Table 1 Activities in CO oxidation (under conditions indicated in the text)

| T/K | t/min | Conversion of CO (%) | Activity/molecules (Pt _s) ⁻¹ min ^{-1a} | |
|-------|-------|----------------------|------------------------------------------------------------------------|---------------------|
| 424.1 | 20 | 8.72 | 0.26 | Pt/SiO ₂ |
| 423.6 | 30 | 11.52 | 0.34 | |
| 423.2 | 40 | 17.80 | 0.52 | |
| 424.4 | 10 | 19.47 | 1.97 | Pt/SnO _x |
| 421.5 | 20 | 29.23 | 1.79 | |
| 420.5 | 30 | 38.27 | 2.35 | |
| 420.5 | 40 | 30.97 | 1.90 | |
| 424.4 | 50 | 43.15 | 2.62 | |

^a Calculated from H₂ adsorption capacities, assuming H/Pt_s = 1.

stream consisted of 1.64 kPa CO and 1.78 kPa O₂ (balanced to 101 kPa with N₂) and flow rate 21.1 cm³ min⁻¹. However, for *in situ* FTIR, the flow consisted of 1.67 kPa CO and 1.86 kPa O₂. Rates of CO oxidation were measured in a flow system after reduction in H₂ at 423 K for 30 min and flushing with N₂ at the same temperature for 10 min. Gas chromatography was used to determine CO₂ concentrations at 10 min intervals.

A Spectra-Tech FTIR-PLAN microscope was used in conjunction with a Perkin-Elmer 1710 FTIR spectrometer. Reflectance IR spectra were measured with a resolution of 8 cm⁻¹ within a field of view of 795 μm and are shown in a difference mode (*i.e.* spectra for the catalysts in the absence of CO were subtracted).

Table 1 shows the activities obtained in CO oxidation as rates of CO conversion per surface Pt atom obtained by taking into account the Pt loading and the Pt dispersions measured by H₂ chemisorption at 195 K. The dispersions of the Pt/SiO₂ used here are documented elsewhere.⁵

Thus, the activity in molecules (Pt_s)⁻¹ min⁻¹ for Pt/SnO_x is substantially higher than that for Pt/SiO₂ at 423 K; alternatively each hydrogen chemisorption site has a higher activity on Pt/SnO_x than on Pt/SiO₂.

CO catalysis and chemisorption on the Pt/SiO₂ gave a peak at 2080 cm⁻¹, which corresponds to linearly bound CO. Catalysis and chemisorption of CO on Pt/SnO_x also gave the 2080 cm⁻¹ band, but in addition a band at 2168 cm⁻¹ (see Fig. 1) that was not restricted to specific areas of the catalyst surface (*i.e.* it existed when many different areas of the catalyst surface were probed using the IR microscope although its relative intensity compared to the 2080 cm⁻¹ band raised with spatial position). No strong evidence for bridge-bound CO was found.

During CO chemisorption bands at 1740, 1703, 1580, 1535, 1475, 1440 and 1340–1320 cm⁻¹ were also observed. In contrast during CO oxidation on Pt/SnO_x bicarbonate bands at 1775, 1726, 1676, 1580, 1490–1440, 1320–1300 and 1275 cm⁻¹ were observed, possibly being due to adsorption of product CO₂ on the hydroxylated SnO_x.⁶

Other researchers⁷ have observed peaks at 2125 cm⁻¹ for adsorbed CO that have been attributed to physically or weakly adsorbed CO at Rh⁺ or Pt^{x+} sites. Bands for chemisorbed *gem*-dicarbonyl species of CO [at 2100 and 2030 cm⁻¹, which are similar to those seen by others, *e.g.* Rh⁺(CO)₂]⁸ have also been observed. It seems that these assignments and species are relevant to the case of CO on Pt/SnO_x. Furthermore, gaseous CO exhibits an IR band at 2143 cm⁻¹. We assume that the band observed at 2168 cm⁻¹ is due to weakly held CO but desorption studies would be needed to prove this. The band is certainly not observed for SnO₂ alone. The involvement of the species responsible for this peak in catalysis is suggested by the modification in its peak shape (*i.e.* it is flattened and broadened) after sustained catalysis.

Therefore, in addition to bicarbonate species⁹ known to exist on SnO_x, micro-FTIR has for the first time revealed weakly held CO on Pt/SnO_x, this may be related to accelerated rates of catalysis; this is an important finding.

Interestingly, the higher turnover number for CO oxidation over Pt/SnO_x than for Pt/SiO₂ may arise from suppression of hydrogen chemisorption by SnO_x since total activities per unit weight are rather similar for Pt/SnO_x and Pt/SiO₂.

Received, 8th January 1990; Com. 0/00132E

References

- D. A. Dowden, *Annual Reports on Progress of Chemistry C in 1979*, RSC, 1980, **76**, 3.
- A. Crossley and D. A. King, *Surf. Sci.*, 1977, **68**, 528; *Surf. Sci.*, 1980, **95**, 131; S. R. Bare, P. Hofman and D. A. King, *Surf. Sci.*, 1984, **144**, 347; R. P. Eischens and W. A. Pliskins, *Adv. Catal.*, 1958, **10**, 1; G. Blyholder, *J. Phys. Chem.*, 1964, **68**, 2772.
- G. C. Bond, L. R. Molloy and M. J. Fuller, *J. Chem. Soc., Chem. Commun.*, 1975, 796.
- Closed Cycle Frequency-Stable CO₂ Laser Technology*, NASA Conference Publication 2456, 1987; D. R. Schryer, B. T. Upchurch, J. D. Van Norman, K. G. Brown and J. Schryer, *J. Catal.*, 1990, **122**, 193.
- A. Frennet and P. B. Wells, *Appl. Catal.*, 1985, **18**, 243.
- E. W. Thornton and P. G. Harrison, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 461.
- J. Y. Yates and G. L. Haller, *J. Phys. Chem.*, 1984, **88**, 4660; F. Boccuzzi, A. Chiorino and G. Ghiotti, *Surf. Sci.*, 1989, **209**, 77.
- J. Bilhou, V. Bilhou-Bougnol, W. F. Graydon, J. M. Bassett, A. K. Smith, G. M. Zanderighi and R. Ugo, *J. Organomet. Chem.*, 1978, **153**, 73; M. G. Wells, N. W. Cant and R. G. Greenler, *Surf. Sci.*, 1977, **67**, 541.
- E. W. Thornton and P. G. Harrison, *J. Chem. Soc. Faraday Trans. 1*, 1978, **74**, 2597.