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Quantitative Infrared Spectroscopy of CO Adsorbed on Pt/SiO_2 Preparations with Different Metal Particle Sizes

In recent work (*1*) we used infrared spectroscopy to follow the rate of oxidation of carbon monoxide adsorbed on Pt/SiO_2 catalysts with different metal crystallite sizes. In order to convert from spectral measurements to rate and compare results for different samples it was necessary to establish: (a) if bandshape and position were particle size dependent, and as a corollary (b) whether a calibration curve determined for one particular sample disk could be applied to other disks of the same or different catalysts.

The current literature (*2–10*) is equivocal on both counts. For carbon monoxide adsorbed on Pt/SiO_2 peak frequencies for linearly adsorbed carbon monoxide are usually stated to be coverage dependent with values from as low as 2030 cm^{-1} to above 2090 cm^{-1} (*5–8*). Integrated molar intensities ranging from 48×10^{-18} (*16*) to 120×10^{-18} cm $molecule^{-1}$ (*9*) have been reported and are thought to depend on peak frequency (*6*). Extinction coefficients show similar variations and have been stated to increase with coverage (*4*) or to decrease with coverage (*7*). Here we report spectral parameters for carbon monoxide adsorbed on two Pt/SiO_2 preparations with different metal particle sizes under conditions appropriate to kinetic measurements.

The basic experimental details were similar to those described elsewhere (*1*). In essence infrared spectra of pressed disks of Pt/SiO_2 were recorded with a Perkin–Elmer model 580 infrared spectrometer operating with a spectral slitwidth of 3.7 cm^{-1} between 2140 and 2000 cm^{-1}. Paired pieces from the same pellet were contained in identical cells of the *in situ* type located in sample and reference beams, thus providing a substantially flat background. The spectra shown later were recorded at temperatures in the range 39 to 65°C and have been corrected for any small residual background point by point subtraction. Two Pt/SiO_2 preparations with different metal particle sizes were studied. Details of their composition and of the disks of each used in much of the work are given in Table 1. The initial pretreatment and equilibration of each sample disk were as described previously (*1*). The quantity of CO corresponding to each spectra was determined either by stepwise addition of gas-phase CO to an oxygen-covered surface and measurement of CO consumed and CO_2 evolved or by stepwise oxidation of adsorbed CO and measurement of CO_2 evolution. Pressure measurements were made with a capacitance manometer (MKS Inst.). This calibration method closely followed the procedure of the kinetic measurements.

Figure 1 shows examples of spectra of CO adsorbed on the two Pt/SiO_2 disks. To permit direct comparison of bandshapes at identical coverage the spectra have been normalized by dividing absorbance by Pt_s, the number of surface platinum atoms per square centimeter of disk (as estimated from hydrogen chemisorption). The peak frequency was slightly lower for the sample with the smaller Pt particle size but bandshapes and heights were closely comparable. The width at half-height decreased with increase in coverage and for all samples could be represented by

$$\Delta\nu/\mathrm{cm}^{-1} = -213.4 - 13.4 \log(\mathrm{Absorbance}/\mathrm{Pt_s}). \quad (1)$$

Figure 2 shows a plot of normalized band area versus CO coverage (defined as Θ_{CO} =

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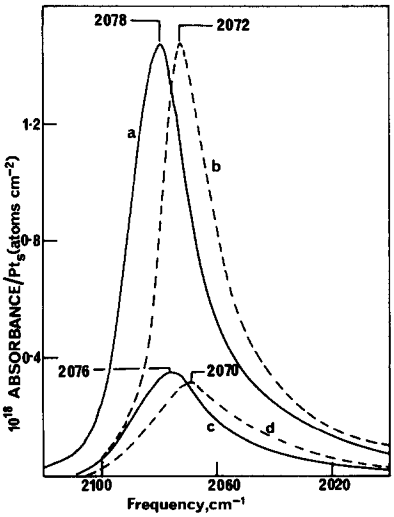

FIG. 1. Spectra (in the form absorbance/Pt$_s$) for CO adsorbed on 5% Pt/SiO$_2$ (solid lines) and 0.5% Pt/SiO$_2$ (broken lines) at the following CO coverages: (a) 0.65; (b) 0.65; (c) 0.20; (d) 0.19.

molecules CO per cm^2 of disk/Pt$_s$). The plots are linear for both samples but do not pass exactly through the origin possibly due to the initial adsorption of a small amount of CO in a form not contributing to the absorption band. The slopes of these plots correspond to the respective integrated molecular intensities which are

$$\bar{A} = 71 \times 10^{-18}\text{ cm molecule}^{-1} = 43 \times 10^{6}\text{ cm mol}^{-1} \quad \text{for 5\% Pt/SiO}_2,$$

$$\bar{A} = 85 \times 10^{-18}\text{ cm molecule}^{-1} = 51 \times 10^{6}\text{ cm mol}^{-1} \quad \text{for 0.5\% Pt/SiO}_2.$$

The difference is barely outside the experimental error but does conform to claims that lower peak frequencies give higher values for $\bar{A}$ (*6*).

Plots of peak absorbance versus molecules adsorbed per unit area for the two samples are given in Fig. 3. The plots are neither linear nor near-coincident. This also applied for disks of the same preparation but differing in thickness and is brought about because a given quantity adsorbed gives coverages and consequently halfwidths which vary with sample thickness and available surface platinum. Correspondence of the curves can be obtained by normalizing both axes by Pt$_s$ as shown in Fig. 4. Coverage by linearly adsorbed CO can then be calculated from absorbance using the equation

$$\theta_{CO} = 1.72 \times 10^{16}\,(\text{Absorbance/Pt}_s)\,[-213.4 - 13.4 \log(\text{Absorbance/Pt}_s)] \quad (2)$$

which is represented by the broken curve. This method provides high precision in the conversion and was used to obtain the values for θ_{CO} reported in our earlier work (*1*). The curvature of Figs. 3 and 4 indicates that extinction coefficients increase with coverage (from $\epsilon_{CO} = 1.5 \times 10^{-18}$ cm^2 molecule^{-1} when $\theta_{CO} = 0.1$ to 2.0×10^{-18} cm^2 molecule^{-1} when $\theta_{CO} = 0.4$). The most recent value for reasonably comparable conditions is 2.5×10^{-18} cm^2 molecule^{-1} as given by Miura and Gonzalez (*11*) at somewhat higher average coverages.

Our measurements contrast with many others in failing to show any significant increase in peak frequency with coverage. As we have previously argued (*1*) this is related to our experimental procedure (cycling between O$_2$ and CO) which results in Pt particles being mainly covered by carbon monoxide *or* oxygen but not both. The relatively high and constant peak frequency we observe is then a consequence of strong dipole–dipole interactions between carbon

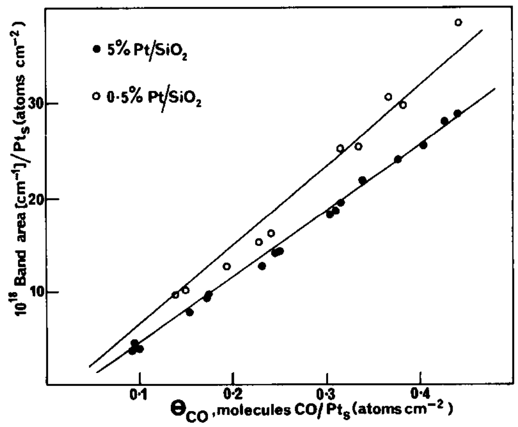

FIG. 2. Band area/Pt$_s$ as a function of θ_{CO} for CO adsorbed on 5 and 0.5% Pt/SiO$_2$.

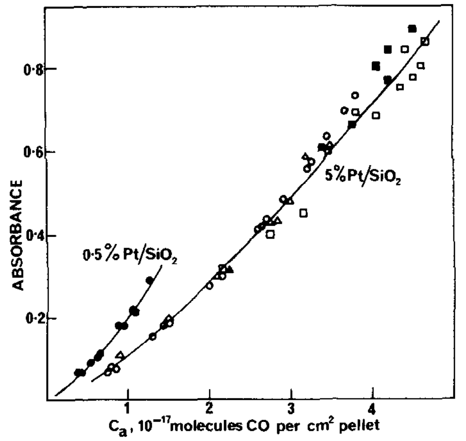

FIG. 3. Absorbance as a function of molecules per unit area of pellet for CO adsorbed on 5.0 an 0.5% Pt/ SiO_2. Different symbols refer to replicate experiments.

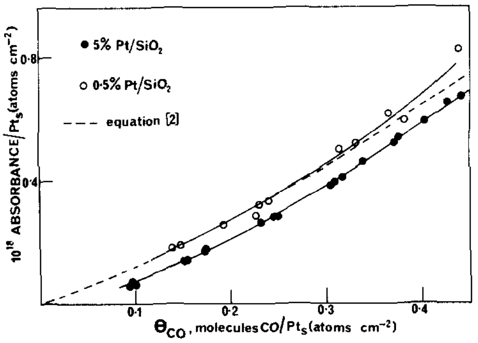

FIG. 4. Absorbance/Pt_s as a function of θ_{CO} for CO adsorbed on 5 and 0.5% Pt/SiO_2 compared to Eq. (2).

monoxide molecules at high local coverage (*5*). The effect is akin to island formation on Pt single crystals (*12*).

If this interpretation is correct then the surface coverage, θ_{CO}, defined previously is a rather curious one. It does not represent uniform and random coverage of all sites on all particles. Rather it represents a combination of the fraction of particles completely covered by CO together with partial coverage of others but always in the form of extensive patches. This is a fortunate situation since for random adsorption, increasing coverage by filling in vacant sites would be accompanied by increasing dipole–dipole coupling effecting not only peak frequency but probably intrinsic adsorption intensity per CO molecule (*12*). The assessment of coverage from spectral measurements would be correspondingly more difficult. The somewhat larger half-width we find for lower θ_{CO} can be attributed to underlying site heterogeneity and possibly smaller patch size on partly covered particles. The presence of substantial heterogeneity is certain since the half-

TABLE 1

Details of Pt/SiO_2 Preparations and Samples of Each Used for Spectral Studies

	Sample 1	Sample 2[a]
Weight percentage Pt	5	0.5
Type of silica	Aerosil (Cab-O-Sil HS5)	Wide-pore gel (Davison grade 62)
Percentage Pt atoms exposed[b]	18	63
Inferred metal crystallite size (nm)	6	1.6
Pellet dimensions (mm)	18 × 8	18 × 8
Pellet weight (mg cm^{-2})	31	29.5
Surface Pt atoms per unit area of pellet, Pt_s (atoms cm^{-2})	8.6×10^{17}	2.9×10^{17}

[a] Preparation designated 63-SiO_2-IonX-S by Uchiyama *et al.* (*16*).

[b] As found by hydrogen chemisorption at 0°C (*1*).

widths reported for adsorption on single crystals (*13, 14*) are one-half or less than those found here.

Recently Bartok *et al.* (*15*) reported substantial apparent hysteresis in peak frequency and half-width (and with less certainty in intensity as well) between adsorption and desorption of CO on Pt/SiO_2. Under these conditions the relationship between adsorption intensity and quantity adsorbed is likely to be complex. Nevertheless, the results here show that under kinetic conditions the spectral characteristics of CO adsorbed on Pt/SiO_2 do not vary greatly with metal particle size or coverage. In consequence a single equation such as (2) coupled with a knowledge of available site number is all that is required to convert absorbance directly to coverage for such samples. A corresponding equation based on integrated intensity (e.g., $\Theta_{CO} = 1.28 \times 10^{16}$ band area/Pt_s as here) may be preferable if changes in half-width with coverage are more complex.

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