

Correlation between CO frequency and Pt coordination number. A DRIFT study on supported Pt catalysts

M.J. Kappers and J.H. van der Maas

*Department of Analytical Molecule Spectrometry, Faculty of Chemistry, University of Utrecht,
P.O. Box 80083, 3508 TB Utrecht, The Netherlands*

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The infrared stretching frequencies of linear-bonded carbon monoxide on face, edge and corner atoms have been identified with four platinum catalysts. The metal particles were supported on different absorbentia and each having a different average particle size, ranging from about 10 to 200 Å. The $\bar{\nu}_{\text{CO}}$ values of the various absorption bands correlate linearly with the number of nearest neighbours of the different surface sites (n in C_n). Effects of an interaction between Pt clusters and support on the linear-CO stretching frequency have not been observed. This empirical correlation between $\bar{\nu}_{\text{CO}}$ and C_n , and the advantages of *in situ* Diffuse Reflectance Fourier transform Infrared Spectroscopy in combination with derivative spectrometry opens the possibility to monitor the dispersity of supported platinum in a simple and relatively quick way.

Keywords: FTIR spectroscopy; diffuse reflectance; supported platinum; CO adsorption; metal coordination number

1. Introduction

Many studies have been carried out on the infrared spectrum of carbon monoxide on supported Pt [1–7]. It was found for instance that the frequency of the stretching vibration of linear-bonded CO increases with the metal particle size. One should be able to use this frequency dependence therefore to estimate the dispersity of the catalyst, but no accurate correlations have been found so far [7]. The surface heterogeneity of the metal particles can be one of the reasons of this deficiency. The maximum of the intense linear-CO band depends on the relative number of the faces, edges and corners of the crystals. Blyholder's model supports this geometric effect that the more unsaturated sites (having the lowest coordination number) as edges and corners will have the lowest CO

frequencies. The metal surface site saturation is given by the coordination number (n in the C_n notation), that is, the number of nearest metal neighbours, ranging from corner atoms with only $n = 3$, to atoms in (111) orientation faces with $n = 9$ [8]. The metal atoms in the crystal faces with high n and low electron density would give little back-bonding from the metal d orbital into the π^* antibonding orbital of CO and hence higher CO frequencies. This must be the reason that comparison between CO absorption bands on supported Pt particles and on single-crystal surfaces is most successful when the metal particles in the catalyst are large with well defined crystal faces.

The absorption band of linear-bonded CO is usually too complex to determine the number of overlapping bands and their position directly. To extract this information from the composed band we have used derivative techniques. The second derivative of a Lorentzian function has a negative lobe which coincides with the position of the maximum of the band and two weaker positive lobes located at wavenumber values equal to the halfbandwidth (HBW) values of the original band. The HBW of the negative peak of the second derivative is a factor of 3 smaller than that of the original band. This effect and the ability of derivative spectra to discriminate against broader bands [9–11] offers us the potential to estimate the number and position of the components in a composite CO band.

In a previous investigation on the adsorptive behaviour of CO on standard 6.3 wt.% Pt/SiO₂ catalyst EUROPT-1 we found (with derivative techniques) two CO components in the wavenumber region from 2095 and 2073 cm⁻¹ which could be assigned to CO molecules adsorbed on the (111) and (100) crystal planes of the supported metal particles [12]. An attempt to analyse the rest of the broad CO band, i.e. to assign the different absorptions to the individual edge and corner sites failed because of strong overlap of the components.

The solution of this problem, however, lays in the investigation of the CO stretching frequency on well-defined Pt-catalysts differing in crystallite size, and it forms part of the results reported here. Results obtained at elevated temperatures and the interaction of O₂ + CO will be reported elsewhere [13].

2. Experimental

The investigated systems were a home-made 10 wt.% Pt/SiO₂ catalyst, the EUROPT-1 (6.3 wt.% Pt/SiO₂) [14–19], the EUROPT-3 (CK303) catalyst (0.3 wt.% Pt/CK300) and a 1.2 wt.% Pt/K-L zeolite. The home-made 10 wt.% platinum catalyst was prepared by impregnation of silica hydrogel spheres with an aqueous solution of chloroplatinic acid. This catalyst was reduced *ex situ* in pure hydrogen at 973 K for 20 h. The 1.2 wt.% Pt/K-L zeolite was purchased from T.U. Eindhoven, the Netherlands. The catalyst samples were carefully ground in an agate mortar and pestle to get a fine powder.

Table 1
Some catalyst parameters

Catalyst	Dispersion (%) ^a	Average particle size (Å) ^b	Number of atoms per crystallite	Coordination number of atom sites [8]
10 wt.% Pt/SiO ₂	13	200	> 3.10 ⁵	9,8
6.3 wt.% Pt/SiO ₂	64	16	13, 55, 147 ^c	8,7,5
0.3 wt.% Pt/Al ₂ O ₃	100	< 15	~ 13 ^d	7,5
1.2 wt.% Pt/K-L	100	< 15	6-8 ^e	5,4,3

^a Data calculated from CO adsorption isotherm (CO:Pt_s = 1).

^b Data determined from TEM results.

^c From [20].

^d From [21].

^e Data calculated from EXAFS results.

The neat samples were reduced in a pre-dried 10% H₂/Ar flow at 673 K for 16 h. This reduction was performed *in situ* in a diffuse reflectance accessory ('Collector', Barnes Analytic) equipped with a standard controlled environmental chamber (Spectra-Tech, model 0030-100). The DRIFT cell was connected to a flow-system suitable for the activation of the catalysts and adsorption of CO. Spectra were recorded on a Perkin-Elmer 1720X FT-IR by coadding 256 scans at 4 cm⁻¹ resolution. Second-order derivative calculations were performed with a 9-points Savitzky-Golay (SG) derivative function on a PE 7500 Professional Computer.

3. Results and discussion

Before coming to the assignments of the various overlapping CO bands we will analyse the structure of the supported platinum crystals in the catalysts. Some relevant properties of the investigated Pt-catalysts are listed in table 1. The statistics of occurrence of atoms with different amount and arrangement of nearest neighbours as a function of the crystallite size has been studied for several crystal structures [8]. These results provide insight into the relative amount of atoms located in faces, edges and corners for the crystallites with dimensions shown in table 1. X-ray [20] and EXAFS studies [21,22] on the EUROPT catalysts and similar systems indicate that the platinum crystals exist as cubo-octahedral units of mainly 13, 55 and 147 atoms in EUROPT-1 and of about 13 atoms in the fcc structure in EUROPT-3. Therefore, the surface of the EUROPT-1 particles will be composed of sites with metal coordination numbers of 9, 8, 7 and 5 (or C₉³, C₈^{4,5}, C₇⁵, C₅⁷ notation as in [8]), whereas in EUROPT-3 the corner or C₅⁷ sites dominate. It seems likely that the cubo-octahedral crystal, bounded by (111) and (100) faces, is thermodynamically preferred in supported

platinum catalysts. Results from TEM indicated that this is also the case for larger particles up to 250 Å in size as the home-made 10 wt.% Pt-catalyst in [23]. The metal particles in the Pt/K-L zeolite on the other hand are so small that the cubo-octahedral morphology cannot be met. Possible structures for crystals as small as 6 atoms may have an octahedral symmetry with $C_4^{9,10}$ atom sites or even a tetrahedral shape for Pt_4 crystals with C_3^9 adsorption sites.

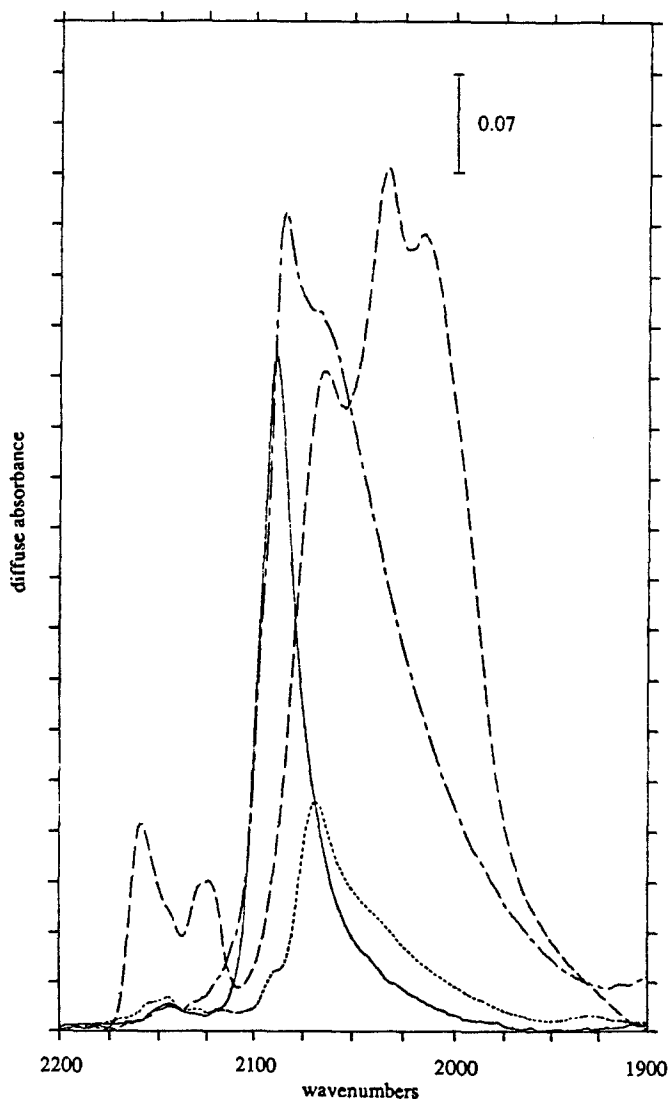


Fig. 1. DRIFT spectra of CO adsorbed linearly in 100% CO atmospheric pressure and RT on: (a) —, 10 wt.% Pt/SiO₂; (b) - - - -, EUROPT-1; (c) ·····, EUROPT-3; (d) - · - · - ·, 1.2 wt.% Pt/K-L zeolite. The spectra have been corrected for catalyst background and CO gas-phase absorptions. The spectra are not normalized for the metallic area.

Fig. 1 shows the spectra of CO adsorbed on the catalyst samples, which were taken in 100% CO at atmospheric pressure. Apart from the CO/zeolite system the spectra show an asymmetrical band in the wavenumber region 2150–1900 cm^{-1} with a weak shoulder at the high frequency side of the maximum and a broad band at the low frequency side. The maxima lie at 2088, 2084, and 2069 cm^{-1} for the HM-catalyst, EUROPT-1 and EUROPT-3, respectively, which shows the aforementioned relation $\tilde{\nu}_{\text{CO}}$ vs. Pt particle size. The spectrum of CO adsorbed on 1.2 wt.% Pt/KL-zeolite shows even five maxima with two peaks above 2100 cm^{-1} and three at 2064, 2033 and 2015 cm^{-1} . The two peaks at 2158

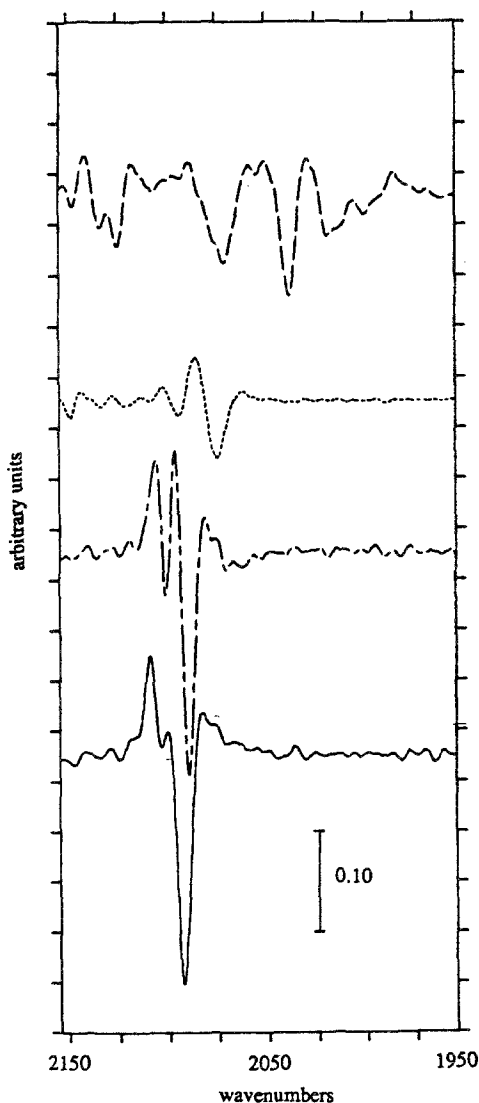


Fig. 2. The corresponding second derivatives of the spectra shown in fig. 1: (a) —; (b) ·-·-·; (c) ·····; (d) - - - - -, using the 9-points Savitzky-Golay method.

Table 2

Second derivative data of linear-CO on the different Pt-catalysts in 100% CO at atmospheric pressure and room temperature

Catalyst	Peak position and (HBW) ^a (cm ⁻¹)					
10 wt.% Pt/SiO ₂	2099 (11)	2089 (15)				
6.3 wt.% Pt/SiO ₂	2096 (11)	2084 (15)				
0.3 wt.% Pt/Al ₂ O ₃		2084 (17)	2058 (25)			
1.2 wt.% Pt/K-L			2063	2034 (21)	2015	1996

^a Values derived from derivative spectra.

and 2126 cm⁻¹ are due to CO adsorbed on oxidized metal sites [1] and will be omitted further on. The CO spectra were further analysed by calculating corresponding second derivatives. The derivative peak positions may not correspond with the original band maxima as a result of band asymmetry. The deviation is estimated to be about 3 cm⁻¹. The derivative results are displayed graphically in fig. 2 with the peak positions and estimated half-bandwidths listed in table 2. It should be noted that the derivative technique discriminates for the broad CO bands at the low frequency side of the maxima. Therefore these cannot be listed in table 2.

Assigning the various band positions to the CO adsorption sites in different environments predicted as in table 1 is straightforward. The positions and HBW's of the CO bands of both silica-supported catalysts is in good agreement with the results for single crystal planes of Pt [1,2]. In view of Blyholder's model we assign the bands at 2096 and 2084 cm⁻¹ to CO molecules located on the (111) and (100) planes of the Pt particles, respectively [12].

The absorption due to CO on (100) surface atoms is also observed (at 2084 cm⁻¹) in the spectrum of EUROPT-3, indicating that the particle size distribution is not homonuclear of Pt₁₃ crystals as suggested for similar alumina-supported catalysts [21]; it contains larger particles. The derivative peak at 2058 cm⁻¹ is assigned to CO bound to the edge sites (C₇) of the metal particles in EUROPT-3. The observation that the CO spectrum of EUROPT-3 is dominated by absorption bands due to the presence of (100) planes and crystal edges suggests that Pt clusters mainly contain 55 atoms with an average particle size of about 11 Å [8].

The CO spectrum of the Pt-zeolite indicates that the particles inside the cages are smaller; the bands at 2063 and 2034 cm⁻¹ are assigned to CO bound to C₇ and C₅ atoms while the ones with lower frequencies must be due to sites with an even lower coordination number.

Fig. 3 shows that the frequencies of the various CO species vary linearly with the number of nearest neighbours of the surface atoms. The infrared data of Kustov et al. [6], who studied the adsorption of CO on three differently prepared Pt/L-zeolite samples are also included in the figure. Their results fit perfectly to the correlation between $\tilde{\nu}_{\text{CO}}$ and C_n.

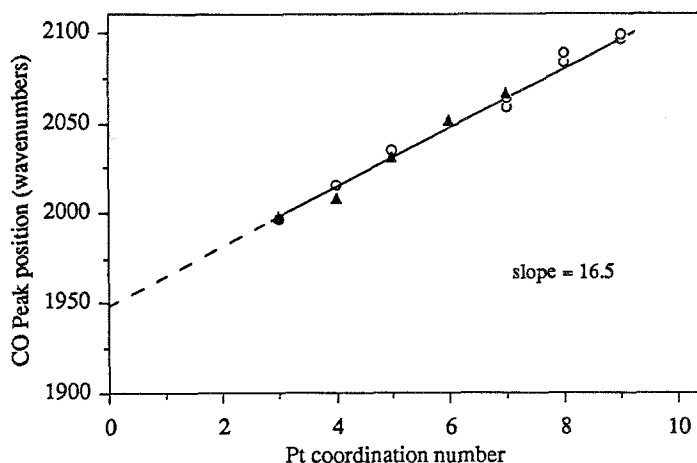


Fig. 3. Variation of the linear-CO derivative peak positions and Pt coordination number of various Pt-catalysts; (○ our data, (▲) from Kustov et al. [6].

The small variations in the value of $\tilde{\nu}_{\text{CO}}$ for the same surface site within the different samples may be the result of difference in dipole-dipole interaction of the chemisorbed CO molecules inherent of the size of the metal clusters or a change of band (a)symmetry. However, on the whole the linearity is quite remarkable. An effect on the underlying support on the infrared frequencies of adsorbed probe molecules has not been observed: consequently, the hypothesis that the electronic modification of the very small metal particles is due to a metal-support interaction in addition to the intrinsic electronic effects should be reconsidered [6,24].

The assignment of a CO absorption band at about 2000 cm^{-1} to CO bound to step sites [3] or more recently to CO interacting with support sites [4–6] seems in view of our results very unlikely. The absence or presence of this band on different catalyst systems must be due to a particle size effect, moreover since we already found evidence for the existence of this 2000 cm^{-1} -band on Pt/SiO₂ [12].

The line in fig. 3 extrapolates at 1948 cm^{-1} at $n = 0$ in C_n , which is much lower than the reported frequency for the matrix-isolated triatomic Pt-CO complex, 2052 cm^{-1} [25]. The difference in the values reflects the different electronic properties of the bulk metal on the one hand, and a single atom on the other. It seems that the properties of bulk platinum will be retained down to very small particle size, i.e. in the size range of the zeolite-supported Pt particles ($\sim 5\text{--}7 \text{ \AA}$).

The frequencies from the Pt-zeolite spectrum corresponding with the surface sites with only 4 and 3 nearest neighbours suggests that either very small metal clusters are present in the zeolite (down to 6 or 4 atoms/cluster) or larger particles of octahedron symmetry with C_7 and C_4 adsorption sites partially

covered by an extra layer of atoms with C₃ sites. Physically it is not impossible that the particles consist of up to 20–30 atoms, since these clusters would still be smaller than the cage dimensions in L-zeolite (12.4 Å). However, the EXAFS results indicate the existence of very small Pt-clusters.

We conclude that the correlation between $\tilde{\nu}_{\text{CO}}$ and C_n opens the possibility to characterize supported platinum on atomic scale, independently of the investigated support of the catalysts. The use of *in situ* DRIFT derivative spectrometry gives the surface scientist a simple and relatively quick technique to monitor the dispersity of platinum catalysts.

We are extending this work by trying to quantify the intensities of the CO bands with curve-fitting procedures.

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