

SHIP-IN-A-BOTTLE FORMATION OF Pd₁₃(CO)_x CLUSTERS IN ZEOLITE NaY

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FTIR spectra of CO adsorbed on gently reduced Pd/NaY show very sharp bands and are markedly different from the familiar broad band CO/Pd/support spectra. New bands are formed when part of the CO is removed. It is proposed that Pd₁₃(CO)_x clusters are formed with singly and multiply bonded CO, including a butterfly configuration. Very similar spectra are obtained, if Pd ions are initially located in the sodalite cages or in the supercages.

1. Introduction

Recently, the detailed mechanism of Pd particle formation in NaY, prepared by the sequence ion exchange/calcination/reduction, has largely been unravelled [1,2]. In particular, specific calcination conditions have been defined which leave the vast majority of the Pd ions *either* in the supercages as diammine complexes, Pd(NH₃)₂²⁺, *or* in the sodalite cages as bare Pd²⁺ ions. In the former case, reduction creates small Pd oligomers which migrate rapidly through the supercage channel system and coalesce to form larger particles. In the latter case, reduction takes place inside the sodalite cages; and at elevated temperatures the Pd atoms migrate into supercages and agglomerate. An open question is, however, whether the reduced metal particles carry memory of their reduction mechanism (as appears to be the case for Pt in NaY [3]) or whether Pd particles of similar size and shape are formed via both routes, e.g. clusters which are smaller than the supercage, but larger than the cage window. Once such particles have been formed and all Pd atoms and smaller oligomers have been consumed, further growth would require high activation energy mechanisms, e.g. Ostwald ripening or local collapse of the zeolite matrix.

In the present research Pd particles have been characterized by adsorbing carbon monoxide and recording FTIR spectra. It is to be expected that spectra of well defined Pd_y(CO)_x clusters, if formed by this ship-in-a-bottle technique, are

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distinctly different from the spectra of CO adsorbed e.g. on SiO₂ supported Pd, reported in the literature [4]. It has been previously found in this lab that Pd/NaY catalysts differ from Pd/SiO₂ by a markedly superior turnover frequency for neopentane conversion [5].

2. Experimental

2.1. CATALYST PREPARATION

2.18 wt% (or 7.30 wt%) Pd on NaY was prepared by ion-exchange of Linde NaY(LZY-52, Lot #968083061080-S-9, Na₅₇(AlO₂)₅₇(SiO₂)₁₃₅.375H₂O). The exchange was carried out by adding a (0.01 M) aqueous solution of [Pd(NH₃)₄](NO₃)₂ (Strem Chemicals, Lot #19167) to a dilute (200 ml/g) zeolite slurry in doubly deionized water and leaving this at 25 °C for 20 hours. Fletcher and Townsend [6] reported that exchange was complete at 25 °C; this was verified by atomic absorption. Our Pd load corresponds to roughly 4 (or 13.4) Pd atoms per unit cell.

2.2. CALCINATION

Calcination was done in pure O₂, at 1 bar and a flow rate of 300 ml/min/300 mg. The temperature ramp was programmed at 0.5 °C/min from 25 °C to the specified calcination temperature (T_c), then held at this temperature for 2 hours. After cooling to 25 °C, 20 mg of the catalyst powder was pressed into a 10 mm diameter wafer. The wafer was then transferred to the IR cell and recalcined at T_c for 10 minutes. O₂ was then replaced by Ar, flushing for 10 min. at T_c . After cooling to 25 °C, the absence of H₂O or OH groups was verified by absence of bands near 1640 cm⁻¹ and 3650 cm⁻¹ [7,8].

2.3. REDUCTION

The wafer was heated from 25 °C to the specified reduction temperature (T_R) at a rate of 8 °C/min, then held at T_R for a specific time (t_R) under flowing hydrogen. The gas was then changed to Ar at T_R for 20 min to remove most of the adsorbed hydrogen. After this reduction the FTIR spectra showed a strong band at about 3650 cm⁻¹, confirming that Pd atoms and H⁺ ions are formed, with the latter occupying cation sites and forming hydroxyl groups.

In this paper we shall use the sample notation Pd_xNaY($T_c/T_R/t_R$), where
 x : number of Pd atoms per unit cell of NaY;
 T_c : Calcination temperature in °C;
 T_R : Reduction temperature in °C, and
 t_R : Reduction time in minutes.

2.4. FTIR MEASUREMENT

The IR spectra were recorded by a Nicolet 60SX single-beam Fourier Transform infrared spectrometer at a resolution of 1 cm^{-1} . Generally, 200 scans were used for each spectrum. A spectrum could be recorded in about 150 s with a good signal/noise ratio. Flowing CO was introduced at 1 bar and 25°C for 10 min.; then the cell was purged with Ar. Background spectra were recorded with a wafer which had not been exposed to CO. The spectra for adsorbed CO were then obtained by subtracting the background.

3. Results

FTIR spectra of CO_{ads} on $\text{Pd}_{13.4}\text{NaY}(500/200/20)$ and $\text{Pd}_4\text{NaY}(250/200/20)$ are shown in fig. 1a and 1b. For identical treatments the spectra are highly reproducible as regards qualitative appearance, band positions and relative band intensities. Bands as narrow and symmetric as those observed in the present study in the region of multiply bonded CO ligands (wavenumbers $< 2000\text{ cm}^{-1}$) are highly unusual for adsorption systems. The band width at half height e.g. of the peaks at 1895 and 1824 cm^{-1} is only 25 cm^{-1} , whereas typical FTIR spectra of CO_{ads} on Pd/SiO_2 – e.g. those reported by Ichikawa et al. [9,10] for average Pd particle sizes of 1.1 nm and 1.4 nm – show only *one* broad peak in this region. Reducing our wafers for 5 hours at 500°C reproduced this familiar broad band spectrum with a half width of 85 cm^{-1} [11].

The new sharp band spectrum of gently reduced Pd/NaY is not limited to sample preparations leaving Pd ions in supercages or to a certain Pd dispersion, as comparison of fig. 1a and 1b shows. The H/Pd ratio was $= 0.43$ for $\text{Pd}_{13.4}\text{NaY}(500/200/20)$, but 0.86 for $\text{Pd}_4\text{NaY}(250/200/20)$ [2]. The highly structured spectra, therefore, suggest that well defined palladium carbonyl clusters are formed and entrapped in the zeolite framework.

The kinetic behaviour of the bands was studied by purging with Ar at 25°C to remove part of the CO. Initially, bands are observed at 2126 , 2120 , 2114 , 1969 , 1956 , 1900 , 1824 cm^{-1} ; their intensity decreases with Ar purging. Peaks at 2102 , 2060 , 1860 cm^{-1} initially increase and later decrease. We, therefore, distinguish an initial *State I* of high CO coverage from the final *State II* of lower CO coverage. Once State II is reached, the spectra do not significantly change by Ar purging at 25°C . The transition from state I to state II appears very similar for both samples.

A strong peak consisting of four overlapping bands is located in the region of terminal CO ligands. The band is centered around 2120 cm^{-1} in State I and shifts to 2102 cm^{-1} in State II. In addition, a weak band develops at 2060 cm^{-1} during CO desorption. In the region characteristic for multiply bonded CO, five bands can be recognized at 1969 , 1956 , 1900 , 1860 and 1824 cm^{-1} . The two bands at

1969 and 1956 cm^{-1} seem to be eroded in concert suggesting that they belong to the same species A. An isosbestic point is located at 2015 cm^{-1} for both spectra. It is therefore tempting to assume that species A, bearing at least two bridging CO ligands, is transformed into a species having one terminal CO ligand.

The bands at 1900 and 1824 cm^{-1} decrease in intensity during CO loss and shift to lower or higher wavenumbers respectively; simultaneously a new band grows in at 1857–1865 cm^{-1} between the original bands. Isosbestic points can be recognized at 1880 and 1840 cm^{-1} , suggesting that a species B with bands at 1900

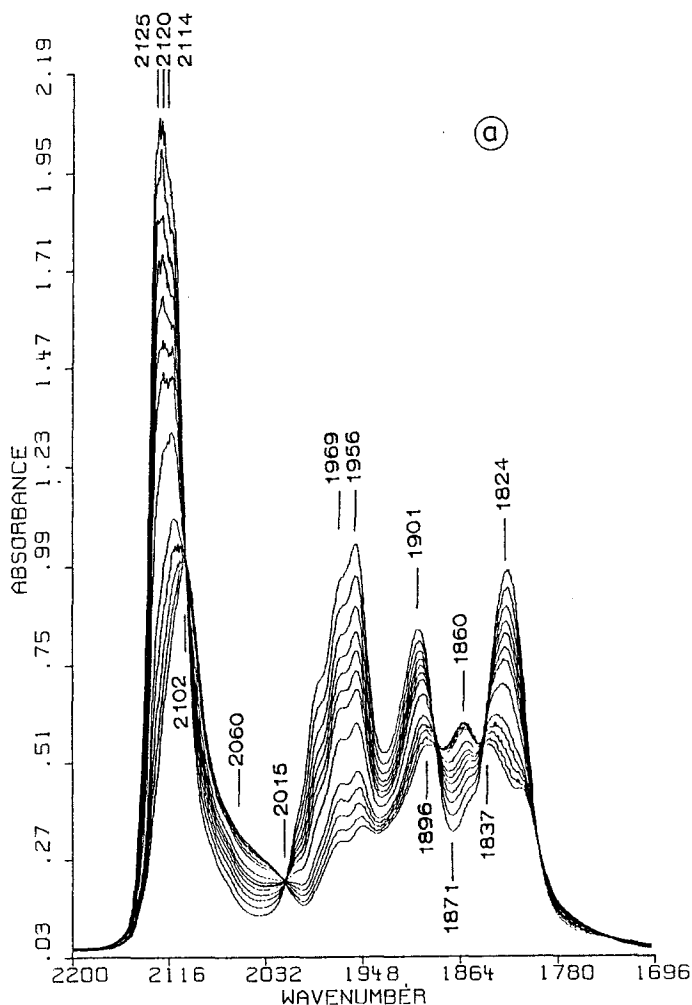


Fig. 1. FTIR Spectra of CO, adsorbed on gently reduced Pd_x/NaY after different purging times with Ar at 25°C.

Fig. 1a. Pd_{13.4} NaY(500/200/20); Purging time (min): 20, 25, 30, 35, 40, 45, 50, 60, 80, 90, 100, 110, 120.

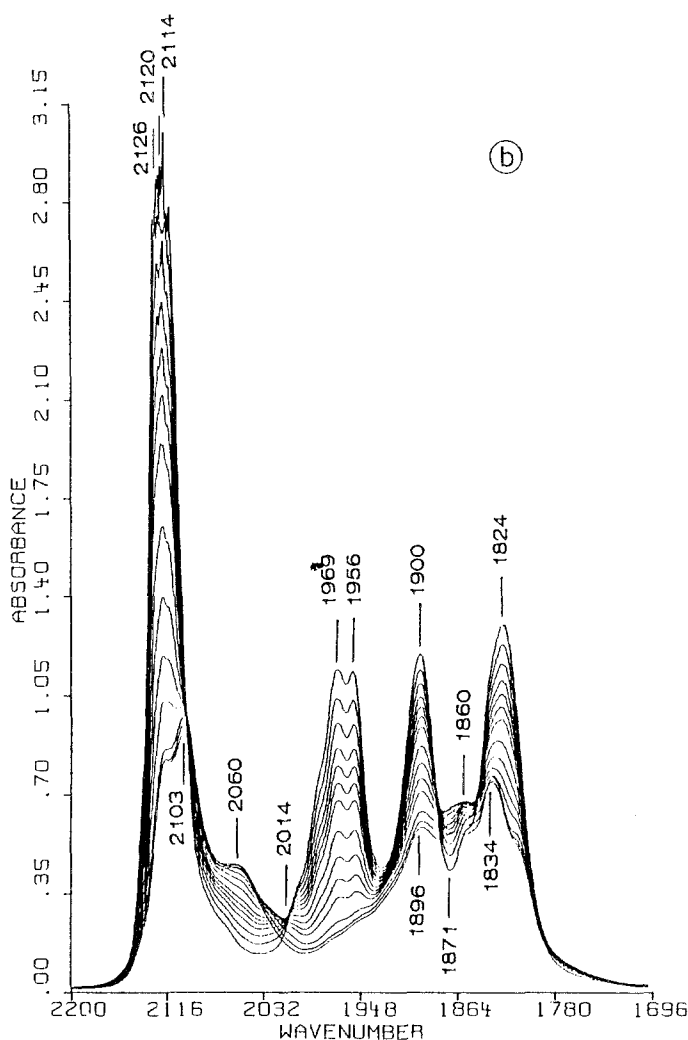


Fig. 1b. $Pd_4NaY(250/200/20)$; Purging time (min): 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 110, 130, 150.

and 1824 cm^{-1} is gradually transformed into a species C, characterized by the band at $1857\text{--}1865\text{ cm}^{-1}$.

Three overlapping bands are observed in the region of terminally bonded CO at 2126 , 2120 , and 2114 cm^{-1} ; they differ in their behavior during CO desorption. The band at 2126 cm^{-1} is most labile and almost vanishes after a 40 min. Ar purge. It is assigned to a Pd^+-CO complex. The band at 2114 cm^{-1} , i.e. at the high frequency border of the range attributed to Pd^0-CO , decreases during CO desorption and is entirely eroded after 80 min. Simultaneously, a new band grows in at 2102 cm^{-1} ; the presence of an isosbestic point at 2102 cm^{-1} suggests a transformation of State I, with characteristic terminal stretching C-O band at

Table 1

Species	State	C-O stretching bands (cm ⁻¹)
A	I	1969, 1956
B	I	2114, 1900, 1824
C	II	2102, 2060(shoulder), 1860

2114 cm⁻¹, into State II with a band at 2102 cm⁻¹. If these assignments are correct, then the band at 2120 cm⁻¹ should be attributed to a Pd^{δ+}-CO complex with the Pd^{δ+} presumably occupying S_{II} sites [12], while the CO ligand may be coordinated to it through the O₆ ring.

The observed Pd_xCO species and the C-O stretching frequencies tentatively attributed to them, are summarized in table 1.

4. Discussion

Evidence from TPR and dispersion measurements by hydrogen chemisorption had suggested that Pd⁰ atoms, once they escape from the sodalite cages, are extremely mobile in the zeolite framework and tend to aggregate into small clusters, which are located in the supercages. A probable structure of these entities is a cluster consisting of 13 atoms, i.e. one center atom surrounded by 12 "surface" atoms. The shape of these clusters might be cubooctahedral (which either hcp or fcc stacking) or icosahedral. Two causes are likely to impede further growth of such clusters: (1) each additional atom will be bonded to only three or four nearest neighbors, whereas the twelve "surface" atoms of the 13-atom cluster have, in the case of the cubooctahedron, five nearest neighbors, or, in the case of the icosahedron, six neighbors at slightly larger distance. (2) A 13 atom cluster is entrapped in the supercage, since its diameter (8.2 Å) is larger than the cage aperture (7.4 Å) [13]; i.e. further coalescence is impossible. Indeed, Bergeret et al. detected 5–7 Å particles in Pd_{13.7}Na_{9.3}H_{19.2}/Y by SAXS after calcination at 600 °C and H₂ reduction at 150 °C [14]. We shall, therefore, assume prevalence of Pd₁₃ clusters which, when covered with CO, are cubooctahedra. To our knowledge no Pd carbonyl clusters have been reported before, suggesting that the zeolite geometry and the "ship-in-a-bottle" preparation are essential for their formation. Reduction at high *T_R* for extended periods will possibly induce formation of larger Pd particles by Ostwald ripening or partial collapse of the zeolite matrix.

The metal atom framework of rhodium cluster anions [Rh₁₃(CO)₂₄H_{5-n}]ⁿ⁻ is known to be a cubooctahedron (hcp stacking) [15,16]; it therefore may serve as a model for the entrapped Pd₁₃ cluster. The carbonyl ligands are doubly bridging and terminal as shown in fig. 2a. The equatorial plane of the corresponding Pd₁₃

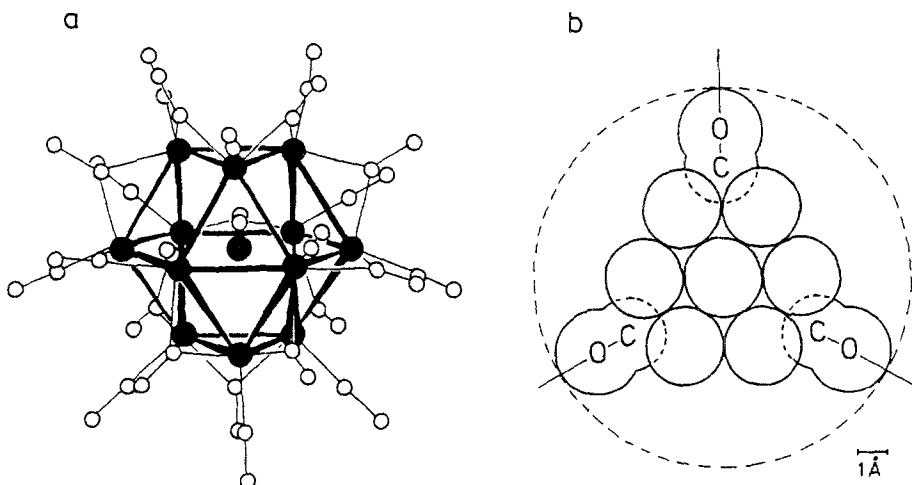


Fig. 2. a. Structure of $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ anions [15,16]. b. Equatorial plane of Pd_{13} cubooctahedron with three bridging CO: $r(PdO)=1.37$ Å; $d(Pd-C)=2.0$ Å; $r(C)=1.3$ Å; $r(O)=1.5$ Å; $d(C-O)=1.15$ Å.

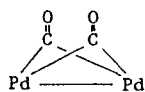
cluster, consisting of seven close packed Pd atoms, is shown in fig. 2b. When CO molecules (three shown) are placed in doubly bridging positions, the adduct exactly fits into a supercage with 13 Å diameter. Terminal CO ligands can be attached to this body in the directions of the four cage windows. Due to constraints imposed by the zeolite structure, the actual CO coordination sphere of this hypothetical Pd_{13} cluster might deviate from that in the Rh_{13} cluster anions, and triply coordinated CO ligands may also be present. In fact, a cubooctahedron with fcc stacking provides eight B_3 sites. Two sets of four such sites have symmetry axes pointing to the corners of a tetrahedron. The tetrahedral arrangement of the four 12-ring windows of every supercage would easily permit coordination of four triply bridging CO ligands on a Pd_{13} cubooctahedron. We thus conclude that a $Pd_{13}(CO)_x$ cluster, located in supercages of NaY, and possessing CO ligands in terminal, doubly and triply bridging positions is entirely consistent with the cage geometry. When fully coordinated with CO (State I), the $Pd_{13}(CO)_x$ cluster is likely to be in the cage center; after partial decarbonylation it may shift towards one of the cage walls, so that particle-wall interactions may become operative in State II. Interaction with the charge balancing cations, Na^+ and/or H^+ , would lead to a polarization of the cluster complex.

Since the pioneering work of Eischens et al. [17] numerous IR data of CO adsorbed on Pd have been published [4]. For assigning the present bands, data of CO on single crystal planes of Pd are of particular interest. As bands on such planar faces generally shift with coverage due to adsorbate-adsorbate-interactions, our interest is focused on data measured near (or extrapolated to) zero coverage, because dynamic dipole-dipole interactions should be negligible for CO adsorbed on very small Pd particles in a zeolite cage. Literature data on Pd(111) show that a band at 1823 cm^{-1} [18] is due to CO in a three-fold coordination site.

Likewise, data on Pd(100) and Pd(210) show that 1895 and 1878 cm⁻¹ bands indicate CO in a two-fold bridging position. Terminal CO shows stretching frequency bands between 2090 and 2112 cm⁻¹ [19,20], viz 2092 cm⁻¹ on (111); 2096 cm⁻¹ on (100); and 2112 cm⁻¹ on a Pd film. Positively charged Pd is revealed by terminal C-O bands \geq 2100 cm⁻¹. Bands at 2125–2130 cm⁻¹ and 2160–2168 cm⁻¹ have been reported for Pd/Al₂O₃ [20,21] and Pd/CeO₂ [21]. They have been assigned to Pd⁺-CO and Pd²⁺-CO, respectively. Juszczyk et al. [22] assigned a 2119 cm⁻¹ band to Pd^{δ+}-CO, i.e. slightly electron deficient Pd atoms.

Interaction force constants are typically small in polynuclear carbonyl clusters, so that the carbonyl spectra are almost exclusively governed by the local symmetry. One, therefore, would expect characteristic wavenumbers for terminal CO, and for CO ligands bonded to two-fold and three-fold Pd sites. The observed band positions, for the highly carbonylated State I, viz. 2114, 1895 and 1824 cm⁻¹, clearly coincide with these three bonding types and are almost identical with the band positions reported for the corresponding species on Pd single crystal faces at zero coverage.

The bands at 1969 and 1956 cm⁻¹ must be attributed to CO ligands in two-fold coordination (species A). As their desorption behavior shows that they belong to one adsorption species, the most probable symmetry is presumably C_{2v}. A pair of Pd atoms with two bridging CO ligands in a “*butterfly*” arrangement, using a pair of Pd atoms, may account for this:



The observed band pair of species A is typical for the highly carbonylated State I. Whether this species is formed on the same cubooctahedron together with the CO ligands which have been described as species B, cannot be concluded from the available data. The partially decarbonylated species C in State II only contains terminal CO, absorbing near 2102 cm⁻¹, and bridging ligands in three-fold coordination sites. As C is presumably in contact with the cage walls and thus with Na⁺ or H⁺ ions, it is interesting that the band of the three-fold coordinated CO ligand is shifted to higher wavenumbers by 30–40 cm⁻¹ relative to that in species B with negligible wall interaction. This shift is consistent with a positive polarization of the cubooctahedron. Note that in molecular cluster anions such as the family of [Rh₁₃(CO)₂₄H_{5-n}]ⁿ⁻ the carbonyl stretching frequencies shift significantly towards lower values as the negative charge increases [23,24].

5. Conclusion

The observed spectra of CO on gently reduced Pd/NaY can be reasonably explained by assuming the formation of cubooctahedral Pd₁₃ clusters in super-

cages. These clusters show little memory of the location of the Pd ions prior to reduction, viz. in supercages or sodalite cages. In the fully carbonylated State I, these cubooctahedra will be located near the cage center, the adsorbed CO is present in terminal, two-fold bridging and three-fold bridging positions. A butterfly arrangement is possible. When partially decarbonylated, the cluster is interacting with the cage walls, this results in an increased stretching frequency of CO ligands in three-fold coordination sites.

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