Intrazeolite large palladium clusters prepared by organometallic chemical vapour deposition†

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Allyl(cyclopentadienyl)palladium was selectively introduced inside the cages of the zeolite NaY *via* chemical vapour deposition in Ar at 25 °C. Palladium clusters were then formed by thermal removal of the volatile ligands under H_2 at 300 °C. High-resolution transmission electron microscopy measurements indicated the formation of large palladium clusters with diameters ranging from 7 to 25 Å. Indirect characterization by IR spectroscopy confirmed that most of the metal is located inside the cages. The existence of entrapped clusters of 25 Å, *i.e.* larger than the zeolite cages, can be explained by a local disruption of the zeolite lattice. The sintering process observed in H_2 at 500 °C is caused by the coalescence of clusters in adjacent cavities, together with a limited migration of palladium atoms resulting in larger external particles. The electronic state and location of the large palladium clusters were studied by Fourier-transform infrared spectroscopy of adsorbed CO molecules. The marked downward shift of the ν_{CO} bands is attributed to the increase in electron density on these clusters. This electron-rich character is due to charge-transfer interactions with the negatively charged oxygen atoms of the cage walls.

Since the early introduction of Pt/KL zeolite catalysts for the selective aromatization of linear alkanes,[1] much work has been devoted to the preparation and characterization of non-acidic catalysts of Pd and Pt as possible alternatives to the classical bifunctional systems for hydrocarbon reforming.[2] The specific behaviour of Pt/KL catalysts is thought to be related to the geometric and electronic properties of metal clusters located inside the linear channels of the zeolite.[3] We have therefore turned our attention to the possibility of preparing palladium clusters inside zeolite cavities in the absence of metal–proton interactions. In fact, the presence of protonic acidity is largely detrimental under catalytic reforming conditions, since fast deactivation occurs *via* coke formation over the acidic active sites. Sheu *et al.*[4] reported the existence of a palladium carbonyl cluster $Pd_{13}(CO)_x$ entrapped in the cages of the zeolite NaY upon admission of CO after reduction at 200–350 °C of ion-exchanged $[Pd(NH_3)_4]^{2+}$, where the size of the cluster is determined by the dimensions of the cage windows.[4] On the basis of the kinetic behaviour of carbon monoxide adsorption/desorption on the entrapped palladium particles the authors proposed that the palladium clusters strongly interact with zeolite protons resulting in positively charged $[H\text{–}Pd_n(CO)_x]^+$ clusters where protons act as anchors for the growing clusters and decrease the electron density on the metal. It is noteworthy that molecular carbonyl clusters of palladium are not known in organometallic chemistry.

In contrast to proton formation with the ion-exchange technique, we have previously developed an organometallic chemical vapour deposition (OMCVD) methodology based on the volatile $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ complex for the preparation of a proton-free Pd/NaY catalyst.[5] The organopalladium complex is introduced inside the Y zeolite cages in the vapour phase and easily decomposed to the metal phase *via* reductive elimination of ligands, without altering the original distribution of positive charges.[5] The activity and selectivity of this sample confirmed the high dispersion and localization of metal particles inside the zeolite channels at the catalytic reaction temperature,[6] so suggesting a quite satisfactory stability towards sintering.

In this paper we report on HRTEM (high-resolution transmission electron microscopy) and FTIR characterization of samples prepared by CVD on both NaY and NaHY zeolites in comparison with previous results on samples obtained *via* ion exchange[4] of $[Pd(NH_3)_4]^{2+}$.

Experimental

The supports utilized were the NaY faujasitic zeolite (Linde type LZ-Y52 U.O.P., Linde Division Batch no. 00621JW), of unit cell $Na_{58}(AlO_2)_{58}(SiO_2)_{134}\cdot 240H_2O$, and a protonated form of it, NaHY, prepared by ionic exchange in a 1 mol dm^{-3} aqueous solution of NH_4NO_3, followed by calcination in air at 500 °C, with a final proton exchange ratio of 60%. The silica (Davison 62, 200 m^2 g^{-1}) was ground, washed with 1 mol dm^{-3} HNO_3, then with distilled water to neutrality and dried. The 2 wt % Pd/SiO_2 was prepared by silica impregnation with $[Pd(acac)_2]$ (acac = acetylacetonate; Aldrich Chemicals Co., batch 00816AY) dissolved in acetone. After subsequent drying *in vacuo*, the solid was calcined in a dioxygen stream at 400 °C for 1 h and reduced at the same temperature in H_2 for 1 h.

The precursor $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ was synthesized according to the literature method.[7] The Pd/NaY and Pd/NaHY samples were prepared by CVD, as previously reported,[5] with a final loading of 2% by weight. The precursor was sublimed in a 6 cm^3 min^{-1} stream of Ar at 35 °C for 24 h onto the zeolite previously heated in 100 cm^3 min^{-1} Ar at 400 °C for 2 h. After the cooling in Ar the samples were heated, in the same reactor, in H_2 from room temperature to 300 °C at 1 °C min^{-1}, left for 1 h at 300 °C and subsequently cooled in Ar. The kinetics of thermal decomposition of the entrapped organometallic precursor has been reported previously.[5,6]

The reduced samples were pressed into 10–20 mg cm^{-2} pellets under an inert atmosphere and placed inside a quartz cell equipped with KBr windows. After outgassing at 100 °C for 30

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Non-SI unit employed: bar = 10^5 Pa.

min the samples were cooled; 100 mbar of H_2 were then admitted to the cell and the samples were heated at 3 °C min^{-1} from room temperature to the reduction temperature T_r (300 or 500 °C) and left at this temperature for the specified period (1 or 3 h). After 20 min of outgassing at T_r, the cell was cooled and transferred to the sample compartment of a Bruker IFS48 Fourier-transform spectrometer. Spectra were recorded at 4 cm^{-1} resolution for an accumulation of 128 scans. The background spectrum was that of the sample immediately after the reduction. The carbon monoxide adsorption/desorption isotherms were recorded by collecting the spectra after each admission of CO from 10^{-3} to 100 mbar at steps of half a decade. A liquid-nitrogen trap was placed in between the gas line and the cell.

At the end of each IR measurement the pellets were ground and the powders dispersed in Pr^iOH in an ultrasonic bath; drops of these suspensions were deposited on perforated carbon grids which, after alcohol evaporation, were inserted in the sample compartment of a JEOL 2000EX high-resolution transmission electron microscope. This instrument operates at 200 kV and reaches magnifications of × 1 200 000. Micrographs of each sample were taken at low (× 150 000–250 000) and at high magnification (up to × 1 000 000) in order to have a complete map of every zeolite grain. The metal particles distribution *versus* diameter for each sample has been obtained for at least 300 counts.

Results and Bands Assignment

Fig. 1 shows the micrographs of Pd/NaY samples after reduction at 300 °C, 500 °C for 1 h and 500 °C for 3 h. Fig. 2 shows the histograms corresponding to the particle size distribution, as measured from the HRTEM images, for each reduction condition. At low reduction temperature (T_r) the distribution shows a bimodal trend with mean diameters of about 10 and 26 Å. At increasing T_r we observe a progressive depletion of smaller components with a parallel increase in larger particles; the mean diameter is, however, nearly constant, ranging between 26 and 29 Å after 3 h at 500 °C. The dispersion data in the histograms show that some large external particles are present at low T_r and that the contribution of small particles is always significant even after 3 h at 500 °C.

The intriguing aspect of these data is that the great majority of visible particles are about twice as large as the faujasitic supercages (d_z = 13 Å). So the question arises whether these particles are really inside the cages or not. In order to verify the metal localization inside the zeolite channels we have performed the following IR indirect characterization: we have compared the overall adsorption of CO palladium particles before and after the admission of molecules, such as H_2O and NH_3, that are able to saturate the zeolite cages but not to adsorb significantly on the external palladium particles. As a reference, the same tests were performed on palladium particles on the 'external' surface in Pd/SiO_2 samples.

Water was first admitted at room temperature to a Pd/NaY sample prereduced at 300 °C and then outgassed for 10 min at room temperature. Under these conditions the cages are filled with water molecules, as indicated by the intense bending band at about 1640 cm^{-1}.[8] Finally CO was admitted up to a final pressure of 100 mbar. The integrated area of the carbon monoxide bands in the IR spectrum was then compared with the corresponding value obtained for adsorption of CO recorded immediately after the reduction. It has been found that, when the cages are filled with water, less than 5% CO is adsorbed. The same test has been undertaken with gaseous NH_3 as the saturating molecule and similar results were obtained. The reference measurements conducted on Pd/SiO_2 provided completely different results: there is no significant difference in adsorption of CO after the pre-admission of H_2O or NH_3 to the SiO_2 surface. Consequently, no appreciable carbonyl bands are observed for our Pd/NaY samples on preventing CO from entering the zeolite cages. This indicates that the contribution from external palladium particles is insignificant.

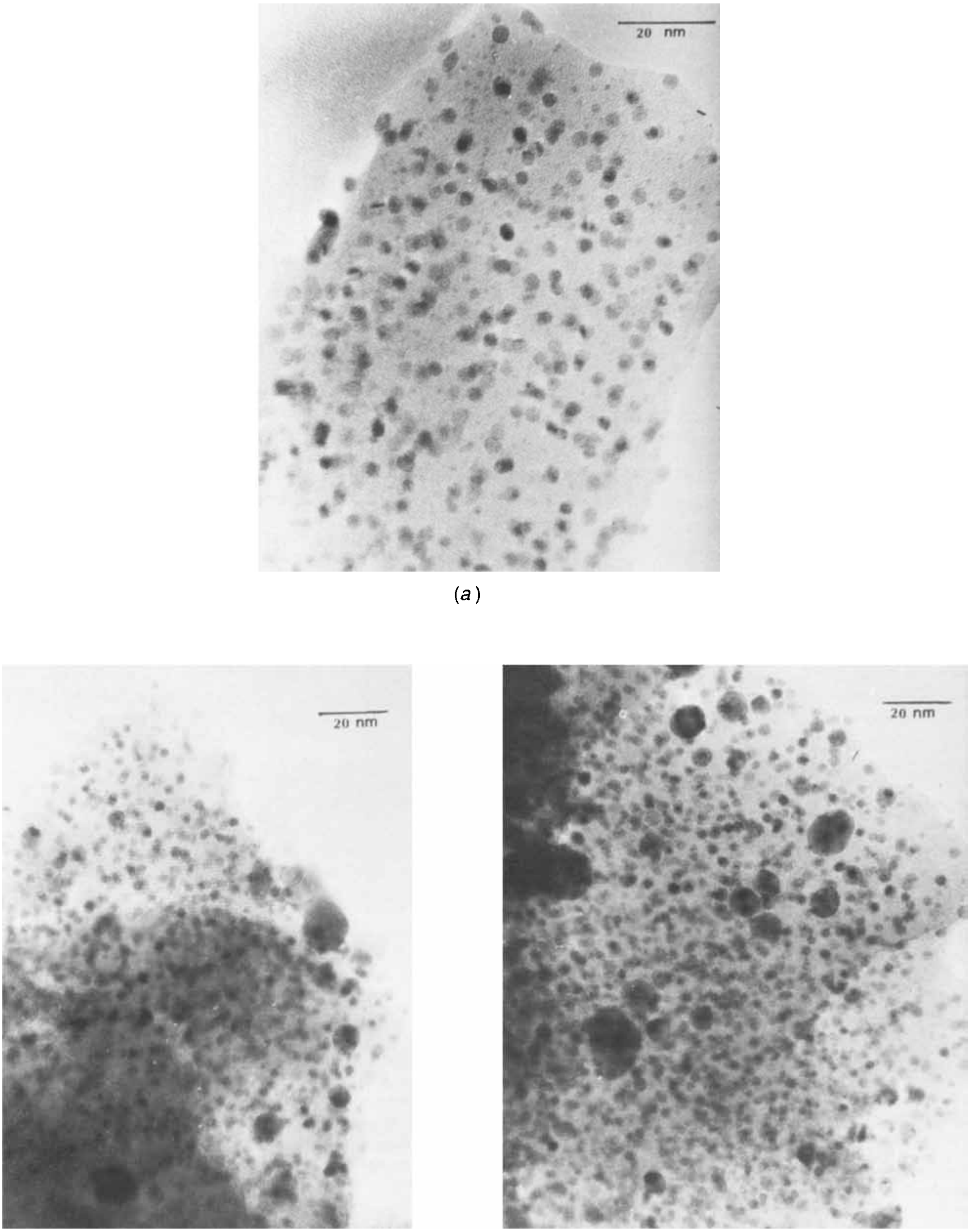
Fig. 3 shows the carbonyl spectra obtained by exposing the Pd/NaY sample reduced at 300 °C to decreasing pressure of CO from 100 to 10^{-3} mbar. The strong band at 2170 cm^{-1} and the shoulder at 2120 cm^{-1} are observed for CO on pure zeolite and could be assigned to molecules of CO interacting with one or two Na^+ ions respectively.[9] These bands readily disappear when decreasing the carbon monoxide pressure by outgassing at room temperature, as a result of the very low adsorption energy.[9] All other absorptions are associated with the presence of palladium and the overall spectral pattern is very different from the highly structured spectra of the sample prepared by ion exchange.[4] In this case there are just two broad and poorly resolved bands, one in the terminal carbonyl region centred at about 2095 cm^{-1}, the other in the bridging carbonyl region at about 1870 cm^{-1}. The carbonyl stretching frequencies are sensibly lower than the corresponding components of the ion-exchange sample and the relative intensity of the linear and bridging carbonyl bands are reversed, the latter being the strongest for the CVD sample. Moreover, the spectra in Fig. 3 appear to move to higher frequencies as the coverage increases. A more detailed analysis of such shifts, which may be associated with various static and dynamic coupling effects,[10] would exceed the scope of this report and will not be considered further. Similar shifts, though smaller, were observed with the ion-exchange samples.[4]

Adsorption of ^{12}CO–^{13}CO mixtures indicates that all the carbonyl bands observed in the spectra are assignable to monocarbonyl species. In fact, each band obtained with pure ^{12}CO has only two components when a ^{12}CO–^{13}CO mixture is employed, which correspond respectively to ^{12}CO and to ^{13}CO (at lower frequencies) monocarbonyl species. Di- and polycarbonyls would generate a much larger multiplicity.[11]

In Fig. 4 the spectrum of the species produced immediately after the admission of 100 mbar of CO to Pd/NaY [Fig. 4(*a*)] is compared with that of the same sample after 14 h of contact [Fig. 4(*b*)]. An intensity redistribution in favour of bridging carbonyl bands occurs, as observed also in the case of Pd/SiO_2, because this is a more favourable energetic situation for palladium surfaces.[12] It can be stressed that this is not a slow diffusion effect inside the pellet, but is due to the transformation of the preformed surface species, as the increasing intensity of the bridging carbonyl bands is accompanied by a decrease in intensity of the less-stable terminal components. Accordingly, only the high-frequency band is drastically reduced in intensity upon outgassing [Fig. 4(*c*)].

Fig. 5 shows the spectra of CO adsorbed at room temperature on Pd/NaY reduced at 500 °C for 1 h under decreasing pressure. An overall reduction of the total area of the carbonyl bands is observed compared to the low-T_r treatment. This effect is certainly related to a lower metal dispersion. However, the position and shape of the main components do not change significantly, in contrast with the behaviour of the samples prepared by ion exchange[4] which have a dramatic dependence on T_r and exhibit spectra more and more similar to those of Pd/SiO_2. The main effect of the high-T_r treatment is to accentuate the band at 1988 cm^{-1}, that was present as a shoulder after the low-T_r treatment (compare Figs. 5 and 3). This is consistent with the HRTEM micrographs showing an increasing contribution of metal particles on the external surface of the zeolite. The low-frequency bridging-carbonyl bands are now centred at 1856 cm^{-1} at highest coverage (Fig. 5), and show the typical behaviour of shifting to lower frequencies upon decreasing pressure of CO (compare Figs. 5 and 3). No relevant modifications in the IR spectra can be observed after long contact time with CO.

In order to find evidence of any role of protons on the adsorption behaviour, we have recorded the spectra of CO



(*a*)

(*b*) (*c*)

Fig. 1 Micrographs of Pd/NaY CVD samples reduced under different conditions: (*a*) 300 °C, 1 h; (*b*) 500 °C, 1 h; (*c*) 500 °C, 3 h

interacting with a sample prepared by CVD (T_r = 300 °C) of a partially protonated NaHY zeolite. The carbonyl spectra (Fig. 6) exhibit an intermediate pattern between those of the proton-free CVD and the ion-exchange samples. All the bands occur at higher frequencies than for the non-acidic CVD sample and the terminal carbonyl components are dominant. The bands of CO adsorbed on Na^+ are sensibly reduced due to the reduced number of Na^+ sites. Moreover, new weak shoulders are observable at higher frequencies (2180–2230 cm^{-1}) due to CO adsorbed on defects, such as extra-frame Al^{3+} defect sites, normally produced by proton exchange.[13] Finally, when reduced at higher T_r, the spectra of the Pd/NaHY sample became similar to those of Pd/SiO_2, as happened with ion-exchange samples.

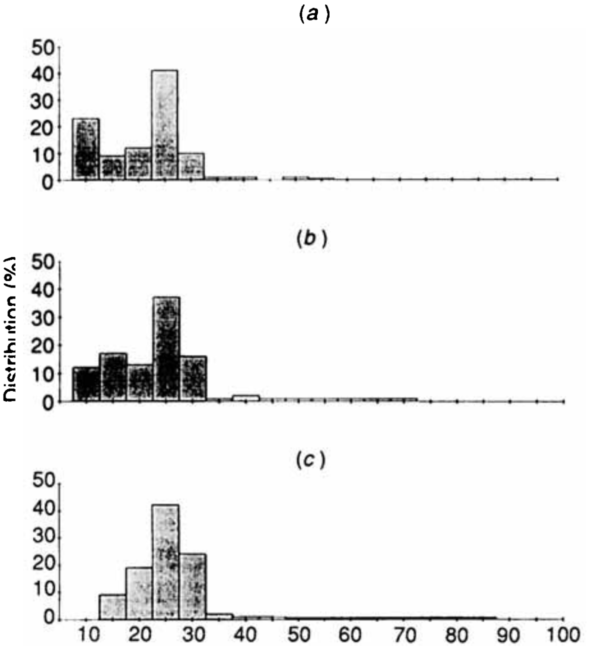


Fig. 2 Particle distribution *versus* diameter for the samples in Fig. 1. Histograms calculated from 300 counts per sample

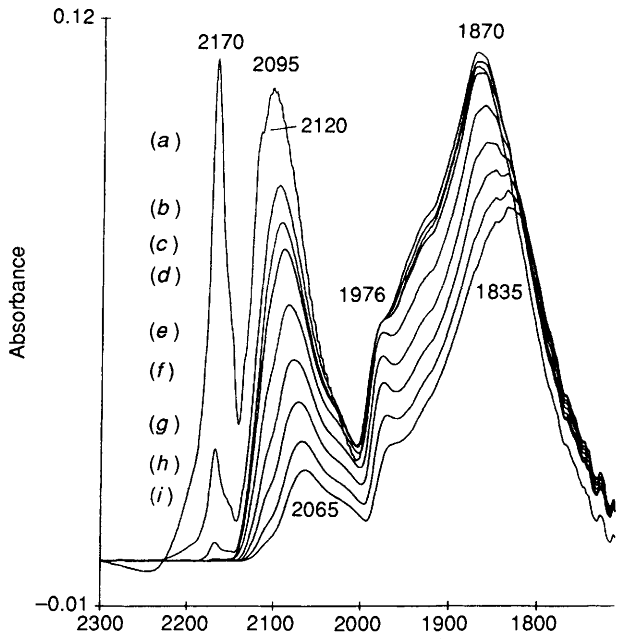


Fig. 3 The FTIR spectra of CO adsorbed on Pd/NaY-CVD-300 at room temperature (r.t.) after admission of 160 mbar of CO and subsequent outgassing at different equilibrium pressures (mbar): (*a*) 100, (*b*) 60, (*c*) 30, (*d*) 10, (*e*) 1, (*f*) 10^{-1}, (*g*) 10^{-2}, (*h*) 10^{-3} and (*i*) pumping for 10 min

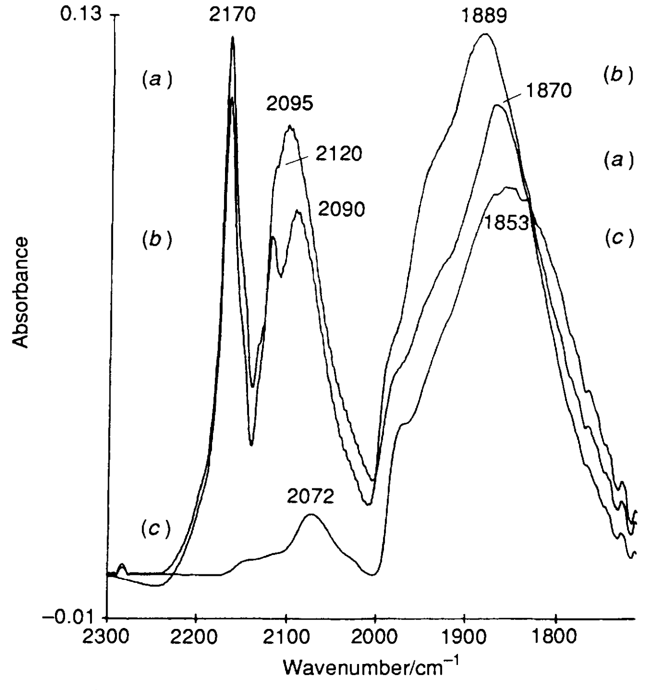


Fig. 4 The FTIR spectra of CO adsorbed on Pd/NaY-CVD-300 at r.t.: (*a*) immediately after the admission of 100 mbar CO, (*b*) after 14 h of contact and (*c*) after outgassing of CO

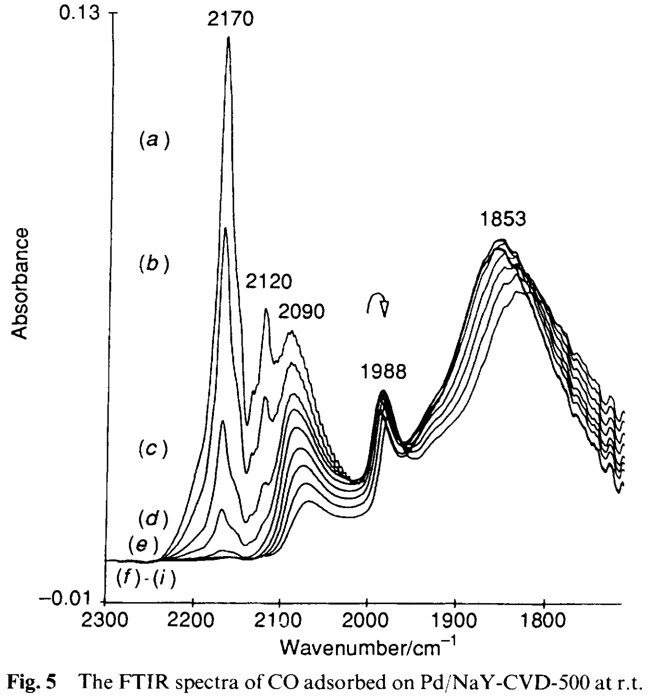


Fig. 5 The FTIR spectra of CO adsorbed on Pd/NaY-CVD-500 at r.t. after admission of 160 mbar of CO and subsequent outgassing at different equilibrium pressures (mbar): (*a*); 100, (*b*) 60, (*c*) 30, (*d*) 10, (*e*) 1, (*f*) 10^{-1}, (*g*) 10^{-2}, (*h*) 10^{-3} and (*i*) pumping for 10 min

Discussion

A somewhat surprising indication from the HRTEM micrographs of the CVD samples is the presence of large metal clusters with mean diameters of about 25 Å (two times larger than the zeolite supercages).* A naked palladium cluster of 25 Å diameter and face-centred cubic packing in cuboctahedral geometry is made up of 300 metal atoms.[14] Are these particle dimensions compatible with the observed metal distribution, or are they due to optical aberrations?[15]

The faujasitic zeolites have a cubic unit cell with $a = b = c = 25$ Å and two complete supercages per cell. At a 2% by weight metal loading, we may assume an average distribution of two Pd atoms per supercage. So, each 300-atoms-large cluster implies 150 empty cages or 75 empty unit cells. In a three-dimensional lattice the mean distance between two neighbouring metal particles is estimated to be 100 Å. Such a value is perfectly consistent with the observed particle distribution (Fig. 1), making us confident that we are observing the actual particle size.

The problem is now whether the zeolite is able to host clusters

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* Here the term cluster is used to refer to a wide range of metal nuclearity, from aggregates of 13 (diameter 7 Å) to 300 atoms (25 Å).

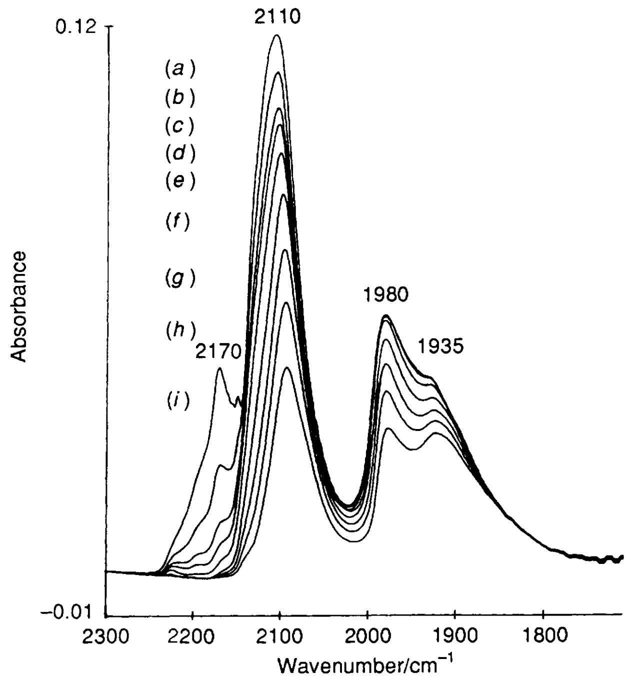

Fig. 6 The FTIR spectra of CO adsorbed on Pd/NaHY-CVD-300 at r.t. after admission of 160 mbar of CO and subsequent outgassing at different equilibrium pressures (mbar): (*a*) 100, (*b*) 60, (*c*) 30, (*d*) 10, (*e*) 1, (*f*) 10^{-1}, (*g*) 10^{-2}, (*h*) 10^{-3} and (*i*) pumping for 10 min

greater than the supercage or if such particles have to stay on the external surface. The results obtained from the cage saturation by various adsorbates before admission of CO seem to confirm that most of the metal is located inside the cages. In fact, when CO is prevented from entering the cavities, no carbonyl bands are observed, confirming that the contribution of the external metal, if any, is negligible. Effects on the adsorption of CO_2, not described here, lead to the same conclusion.

The existence of inner clusters larger than the zeolite cages can be explained by a local disruption of the zeolite lattice. The growth of particles located in adjacent cages can progress until their coalescence with the consequent enlargement and/or disruption of the interconnecting windows. These framework defects would not be revealed by the IR investigation of framework vibrations because the local disruption of crystallinity is of the order of 1–2%, *i.e.* at the limits of the resolution of the spectroscopic technique.

However, after the low-T_r reduction (300 °C) large clusters exactly fitting the cages, with diameters of 7–13 Å, are also significantly present, besides particles resulting from the coalescence of two adjacent filled cages. At increasing T_r, the sintering between neighbour clusters is favoured and in the HRTEM histograms we observe a partial conversion of the smallest components into the larger.

From the spectra in Fig. 3 we can see that the carbonyl IR bands of the CVD sample reduced at 300 °C occur at frequencies somewhat lower than those usually assigned to adsorption of CO on supported palladium.[16] At 100 mbar CO pressure the main components are centred at about 2095 and 1871 cm^{-1} but at lower pressure, *i.e.* in the absence of any coupling effect, these values fall to 2065 and 1835 cm^{-1} respectively. The characteristic ν_{CO} values for linearly bonded CO on dispersed supported Pd (as on Pd/SiO_2) range from 2070 cm^{-1} at low coverage to 2100 cm^{-1} at high coverage;[16] for bridging CO the range is 1980–1900 cm^{-1}.

Such differences deserve some comments as they might contain structural information. It is known that on transition metals the ν_{CO} values decrease with decreasing particle size (due to the enhanced π^*-back bonding) and decreasing coverage.[16] However, the low CO stretching maxima of our samples are not simply assignable to the cluster-size effects because the HRTEM experiment indicates that the mean particle diameter is similar to that for Pd/SiO_2. We explain this behaviour as being related to the existence of metal–support interactions. The carbonyl band frequencies are very sensitive to the electron distribution, and decrease as the negative charge density increases (more basic sites). The intrazeolite large palladium clusters might gain an electron-rich character by charge-transfer interactions with the O^{2-} sites of the cage walls.

The carbonyl spectra obtained after reduction at 500 °C show some decrease in the metal surface area, the total carbonyl area being about 60% of that observed with the sample reduced at low T_r. This sintering process is shown by the HRTEM micrographs to be substantially caused by the coalescence of clusters in adjacent cavities, apart from a limited migration of palladium resulting in larger external particles. The relevant aspect is that the increased reduction temperature has not significantly modified the carbonyl band distribution, and consequently the nature of the metal–support interactions of entrapped clusters, apart from the intensification of the band characteristic of bridging CO on external palladium particles. In contrast, ion-exchange samples are reported to be more sensitive to sintering conditions,[4] as testified by the dramatic effect on the carbonyl absorption spectra of reduction at 500 °C.

These differences between the ion-exchange and CVD methodologies may be correlated to the extent of metal–support interactions under high-temperature conditions, but are not simply related to the presence or absence of protons. Using a model CVD-based Pd/NaHY sample, we have confirmed that the presence of protons actually decreases the electron transfer from the support. However the formation of small hydridocarbonyl palladium clusters, as proposed by Sheu *et al.*[4] for the ion-exchange Pd/NaY sample, is not observed here. Indeed, the use of a charged precursor in the case of the ion-exchange sample may produce a stronger interaction with the support in the first step of the preparation, increasing the number of nucleation centres. In fact, Zhang *et al.*[17] provided evidence for the predominant existence of Pd_6 clusters after mild reduction. The anchoring effect of zeolite protons is thus maximized in the presence of a much larger number of these small clusters.

Conclusion

In this work we have tried to use the combination of HRTEM and FTIR spectroscopy, with CO as probe molecule, for characterizing zeolite-entrapped palladium clusters obtained from OMCVD. The two techniques were in good agreement in revealing the preferential promotion of entrapped palladium clusters with diameters ranging from 7 to 25 Å. In addition, migration of palladium on the external surface is limited also after reduction at higher temperature. The adsorption of CO clearly indicated the electron-rich character of the large entrapped palladium clusters, as a result of electron transfer from basic sites of the NaY zeolite.

In the case of ion-exchange Pd/NaY samples, the palladium clusters are mainly stabilized *via* $Pd-H^+$ interactions[4,18] leading to the formation of small hydridocarbonyl clusters. Such metal–proton interactions are largely lost at higher reduction temperatures, making ion-exchanged samples more sensitive to sintering.

Particular attention has, however, to be paid to the use of CO as a probe molecule, since it can induce surface restructuring[19] on the metal phase upon prolonged contact leading to a more favourable energetic situation for the palladium surfaces.

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