

Influence of pretreatment atmosphere on the nature of silica-supported Pd generated via decomposition of Pd(acac)₂: an FTIR spectroscopic study of adsorbed CO

W. Daniell, H. Landes, N.E. Fouad¹, H. Knözinger*

*Department Chemie, Physikalische Chemie, Ludwig-Maximilians-Universität München,
Butenandstr. 5-13, Haus E, D-81377 München, Germany*

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Abstract

Silica-supported Pd catalysts were prepared through non-aqueous impregnation of silica with palladium acetylacetonate [Pd(acac)₂]. The influence of the pretreatment atmosphere (O₂, H₂, CO, N₂ and vacuum) at 570 K on the decomposition of the metal complex, and on the oxidation state of the resulting supported Pd particles, was investigated by FTIR spectroscopy of adsorbed CO (at 298 K). Under a mildly reducing (CO) atmosphere Pd⁰ metal particles were formed, whereas under oxidising (O₂) conditions Pd²⁺ was also detected. Reduction under H₂ caused the formation of a carbide-like deposit on the silica surface which blocked all Pd sites to CO adsorption. Pretreatment in N₂ and under static vacuum led to decomposition of the acac ligands and subsequent reduction of Pd by evolved reducing components. This resulted in formation of surface Pd species of mixed valence in the former, and dispersed Pd⁰ particles in the latter sample, respectively. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium acetylacetonate; FTIR spectroscopy; CO adsorption

1. Introduction

In recent years, metal acetylacetonates have become viable alternatives to chloride and nitrate ion-containing precursors for the preparation of supported platinum group metal catalysts [1–4]. Supported Pd particles are typically generated by pretreatment of the Pd(acac)₂ precursor (where acac

denotes C₂H₇O₂) at 673 K under oxidising conditions, followed by reduction at 573–773 K under H₂. Although the intimate decomposition mechanism of supported metal acetylacetonates has yet to be investigated, it is generally agreed that thermolysis of the supported metal complex in an oxygen-containing atmosphere leaves the metal as an oxide [5–7], which is then reduced to generate dispersed metal particles. The process is greatly influenced by the nature of both the transition metal and the oxide support [8].

In a review of the thermolysis of supported metal acetylacetonates [6], it was proposed that the nuclearity of the precursor complex may be preserved when the thermolysis of the ligands is achieved under mild conditions and in a controlled atmosphere. In this way

* Corresponding author. Fax: +49-89-2180-7605.

E-mail address: helmut.knoezinger@cup.uni-muenchen.de (H. Knözinger).

¹ Present address: Chemistry Department, Faculty of Applied Science, Umm Al-Qura University, Makkah Al-Mukarrammah, Saudi Arabia.

the generated metal oxide can be maintained in a dispersed state on the support surface. Indeed, results from this laboratory have shown, that an enhanced dispersion of Pd over a mixed $\text{TiO}_2\text{-SiO}_2$ support was achieved when using a $\text{Pd}(\text{acac})_2$ precursor than with a nitrate precursor pretreated under the same conditions [9].

However, a recent study of Pd/SiO₂ catalysts has shown that for decomposition of the acac ligands to be complete a temperature of at least 523 K under oxidising conditions is required, and that pretreatment under a non-oxidising atmosphere (He) leads to formation of a carbonaceous material on the surface, which is not fully removed by reduction [1]. In fact, reduction at 773 K under H₂ forms a carbide-like deposit which blocks the Pd sites, whereas at 523 K the loosely-packed carbonaceous material remains, allowing a proportion of the Pd sites to be catalytically active. It would appear, therefore, that an active surface can be generated under inert conditions, though an oxidising environment is needed to fully remove the organic ligands, in spite of the risk of losing metal oxide dispersion through agglomeration at the higher temperatures involved.

In this study we investigate the nature of silica-supported Pd species generated after pretreatment of the $\text{Pd}(\text{acac})_2$ precursor at 573 K under a variety of atmospheres, ranging from oxidising (O₂), through inert (N₂, static vacuum) to reducing (H₂, CO). Additionally, we ascertain whether the evolution of CO (and other reducing fragments) through the decomposition of the ligands plays a role in the generation of dispersed Pd⁰ particles in an inert atmosphere.

Investigation of the generated Pd/SiO₂ catalysts was achieved through use of FTIR spectroscopy of adsorbed CO probe molecules, a technique well suited to examination of coordinatively unsaturated (cus) cationic and metal sites [10]. CO lends itself to investigation of Pd systems [3,11], being highly sensitive to back donation of electrons from metal d orbitals into its anti-bonding π^* -orbital, resulting in a weakening of the C–O bond and a shift away from the gas phase frequency (2143 cm⁻¹) to lower wavenumbers [12]. Hence, in Pd-containing samples, it is possible to distinguish between CO bonded to Pd²⁺ (4d⁸), Pd⁺ (4d⁹) and Pd⁰ (4d¹⁰) cus sites [13], as well as between terminal and bridged (μ_2 and μ_3) carbonyls [14,15].

2. Experimental

The silica-supported palladium catalyst was prepared via a non-aqueous impregnation route using a palladium acetylacetonate (STREM Chemicals) precursor. Five grams of silica (BASF AG) were pretreated at 670 K in vacuo for 2.5 h, and then suspended in a solution of $\text{Pd}(\text{acac})_2$ (0.174 g) in THF (50 ml) and heated under reflux for 2 h. The organic solvent was subsequently removed and the sample (1.15 wt.% Pd content) dried overnight. Decomposition of the Pd complex was separately achieved before each infrared measurement through in situ thermal treatment in either O₂, H₂, CO or N₂ flow, or under static vacuum.

FTIR spectra were recorded at 1 cm⁻¹ resolution using a Bruker IFS 66 spectrometer equipped with an MCT detector. Samples were pressed into self-supporting disks of ca. 5–10 mg cm⁻² and placed into a purpose-built, high-vacuum infrared cell with attached furnace section, enabling the samples to be pretreated in a range of gas flows or under vacuum. Pretreatment under O₂, H₂, CO and N₂ was carried out at 570 K for 1 h, followed by evacuation at the same temperature for 30 min, before cooling to room temperature and admission of CO. For the in vacuo pretreatment, the cell was firstly evacuated at 370 K for 15 min, and then heated at 570 K under static vacuum (ca. 1×10^{-5} hPa) for 1 h. The evolved gases were removed from the cell under dynamic vacuum at 570 K for 30 min, before cooling the cell to room temperature.

Reduction of the PdO particles generated through pretreatment under O₂ was carried out by heating the sample under an atmosphere of 200 hPa CO at 470 K for 15 min. The cell was then evacuated and cooled to ambient temperature, whereas CO was admitted in increments of 1 hPa and spectra recorded. Spectra are presented after subtraction of the contributions from the gas phase and the solid before CO admission.

3. Results

3.1. Pretreatment under O₂

The IR spectra of adsorbed CO taken after pretreatment in O₂ (570 K, 1 h) are shown in Fig. 1 (spectra (a) and (b)). The carbonyl stretching bands

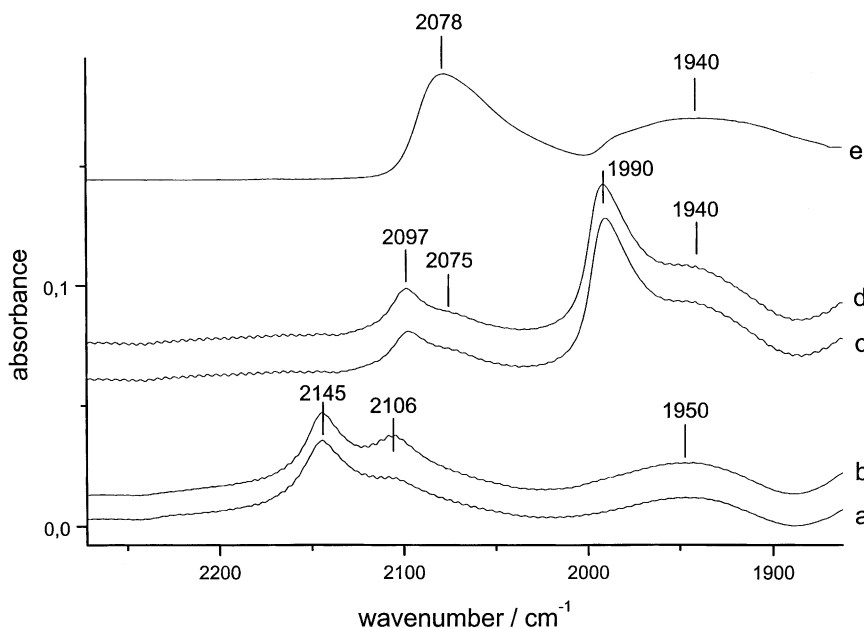


Fig. 1. IR spectra of adsorbed CO after pretreatment under O_2 (570 K): (a) at RT under 100 hPa CO; (b) after 10 min at RT under 100 hPa CO; (c) after secondary reduction treatment (200 hPa CO, 470 K), at RT under 2 hPa CO; (d) under 20 hPa CO; (e) after re-oxidation (O_2 , 570 K) and reduction (200 hPa CO, 470 K), at RT under 30 hPa CO.

(ν_{C-O}) have been assigned to Pd adsorption sites with the aid of results from previous studies on Pd-SiO₂ and Pd-Al₂O₃ systems [11,13,16], and are listed in Table 1. On admission of 10 hPa CO at room temperature (RT), a band at 2145 cm⁻¹ is observed which increases steadily in intensity until saturated under 100 hPa CO (spectrum (a)). This band is attributed to a monocarbonyl Pd²⁺-CO species [13], most likely associated with a PdO phase formed through oxida-

tion of the Pd(acac)₂ precursor. A weak band is also observed at 2106 cm⁻¹, together with a broad, diffuse band with maximum at ca. 1950 cm⁻¹. The former is assigned to CO adsorbed on Pd metal particles (terminal Pd⁰-CO), whereas the latter is attributed to isolated, bridging carbonyls, where a single CO molecule is bound to two Pd⁰ centres [Pd₂-CO (iso)] [11]. After leaving the sample at RT under 100 hPa CO for 10 min, an increase in intensity at 2106 cm⁻¹

Table 1
Assignment of IR bands (ν_{C-O}) for adsorbed CO species [11,13,20]

Pretreatment procedure	Infrared band assignments					
	Pd ²⁺ -CO	Pd ⁺ -CO	Pd ⁰ -CO	(Pd ⁰) ₂ -CO (comp) ^a	(Pd ⁰) ₂ -CO (iso) ^b	(Pd ⁰) ₃ -CO ^c
O ₂	2145		2106		1950	
O ₂ + reduction			2097	1990	1940	
CO			2105	1984	1930	1885
N ₂	2140	2128	2102	1971		
N ₂ + vacuum	2151		2099–2077		1950	
Static vacuum			2095–2070		1930	1880

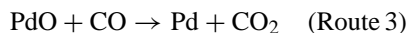
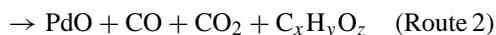
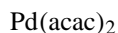
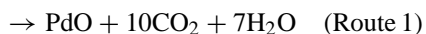
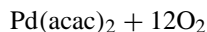
^a Compressed bridged carbonyls.

^b Isolated bridged carbonyls.

^c Triply bridged carbonyls.

is observed (spectrum (b)). However, neither of the two other bands shows either an increase or decrease in intensity. This suggests that the increased number of Pd⁰-CO species does not arise from the reduction of Pd²⁺-CO species, nor from the reversion of bridged carbonyls to monocarbonyl species. A possible explanation is that a proportion of the Pd metal sites are partially covered by carbonaceous debris from the incomplete oxidation of the precursor, which affects diffusion of CO to the Pd surface and retards formation of the Pd⁰-CO species. What is clear, however, is that even after pretreatment under O₂, Pd sites in reduced oxidation state are present on the surface.

These observations concur with Lomot et al. [1] who proposed a decomposition of the Pd(acac)₂ complex to PdO under 1% O₂/He, and observed the evolution of CO and higher hydrocarbon fragments (*m/z* = 57, 85 and 100) as decomposition products. It would appear, therefore, that even under oxidising conditions a total oxidation of the organic ligands, such as proposed in Route 1, does not occur. Instead, decomposition to PdO proceeds via the evolution of CO, CO₂ and a variety of CHO fragments (Route 2). The adsorption of CO (or other reducing fragments) onto the newly generated PdO could lead to reduction and formation of Pd metal (Route 3).



The oxidised sample was then reduced in a CO atmosphere (200 hPa CO) at 470 K for 15 min, before being cooled to RT. On admission of 2 hPa CO (Fig. 1, spectrum (c)) bands at 2097, 1990 and ca. 1940 cm⁻¹ were observed. The bands were assigned to monocarbonyl (Pd⁰-CO), compressed-bridged and isolated-bridged species, respectively [13]. All evidence of PdO particles (2145 cm⁻¹) was removed, indicating complete reduction to Pd metal, though the shoulder at 2075 cm⁻¹ suggests that an in-homogeneous dispersion of Pd particles exists. The compressed-bridged species (1990 cm⁻¹) refers to bridged carbonyl species which are close enough to directly interact with one another, i.e. each Pd centre

is bound to two bridging carbonyls. The appearance of compressed bridging carbonyls has been linked to the preferential exposure of the Pd(1 1 1) face, which is associated with pillbox morphology in larger Pd metal particles [9]. All three bands show a slight increase in intensity with CO pressure but are saturated on addition of 20 hPa CO (Fig. 1, spectrum (d)). The bands at 2097 and 1990 cm⁻¹ both show a slight shift (2 cm⁻¹) to higher wavenumber upon saturation caused by dipole-dipole interactions [12].

Re-oxidation of the sample (570 K, 1 h) under oxygen flow, followed by reduction under CO (as described above) was then carried out. The spectrum on admission of 30 hPa CO at 298 K is shown in Fig. 1 (spectrum(e)). From the overall greater peak intensity it may be proposed that more Pd has been exposed due to increased removal of organic residue from the sample surface. The ratio of the linear to bridged carbonyl species also suggests that the dispersion is also enhanced. The lower wavenumbers observed for the Pd⁰ carbonyl species in this re-reduced sample compared with the oxidised and singly reduced samples, would indicate the presence of some unreduced, electron-deficient Pd species (perhaps Pd⁺) in the latter samples.

3.2. Pretreatment under H₂

After pretreatment under H₂ (1 h, 570 K) the sample takes on a black colouration. Bands at 2964, 2931 and 2862 cm⁻¹ are observed and attributed to (-CH₃) and (-CH₂-) moieties present in a carbonaceous residue, reportedly formed by the incomplete decomposition of the organic ligands under non-oxidising conditions [1]. Admission of up to 100 hPa CO at RT failed to generate any Pd-CO interactions, and so we assume that the Pd sites are blocked. Further reduction under H₂ (570 K, 1 h) leads to the removal of all C-H bands from the spectrum, but CO adsorption at RT again fails to lead to any interaction with Pd. It is now assumed that a carbide-like deposit is covering the surface, as previously reported [1,17].

3.3. Pretreatment under CO

IR spectra of adsorbed CO taken after pretreatment under CO (570 K, 1 h) are shown in Fig. 2. The lower trace (spectrum(a)) is taken at RT after admission of

1 hPa CO. The bands at 2105 and 1984 cm^{-1} are assigned to monocarbonyl and bridging carbonyl species bound to Pd metal, respectively (see Table 1). The two shoulders at 1930 and 1885 cm^{-1} are indications of further bridged carbonyl species. The former is indicative of isolated bridging carbonyls, whereas the latter is associated with three-fold coordinated (i.e. triply bridging) CO [13,14].

A slight increase in intensity of the monocarbonyl band (2105 cm^{-1}) is noted upon admission of 10 hPa CO, whereupon this band is saturated (spectrum (b)).

When a comparison is made between the spectra shown in Figs. 1 ((c) and (d)) and 2 ((a) and (b)), it can be seen that direct reduction of the Pd(acac)₂ precursor under CO at 570 K, yields very similar Pd species to those formed on reduction of the oxidised sample. One point of interest, however, is the difference in intensity ratios between the monocarbonyl and compressed-bridging carbonyl species for the two samples. In the CO pretreated sample (Fig. 2), the ratio in intensity of the two species is roughly 1:1, whereas in the oxidised sample after reduction (Fig. 1c and d), the bridging species (1990 cm^{-1}) is dominant. This suggests a better dispersion of Pd metal particles in the former case, or at least the formation of smaller particles.

3.4. Pretreatment under N₂

Admission of CO after pretreatment under N₂ (570 K, 1 h) leads to the formation of two broad bands with maxima at ca. 2100 and 1960 cm^{-1} . Upon saturation of these bands under 100 hPa CO (Fig. 3, spectrum (a)), the maxima shift to 2102 and 1971 cm^{-1} , respectively. The former band is assigned to the monocarbonyl species and the latter to the compressed-bridging carbonyl species, both bound to Pd metal sites (see Table 1). However, the broadness of the two bands indicates the non-exclusivity of these sites. Indeed, two shoulders are visible within the high frequency band at 2140 and 2128 cm^{-1} , which are assigned to Pd²⁺-CO and Pd⁺-CO monocarbonyl species, respectively [13]. These peaks were identified through deconvolution of the band envelope fitting with both Gaussian and Lorentzian curves using Origin software. The width of the low frequency band (ca. 2000–1900 cm^{-1}) also suggests the presence of more than one type of bridging carbonyl, indicating a non-homogeneous dispersion of Pd metal, perhaps within clusters of agglomerated particles of varying size.

After vacuum treatment at RT for 10 min, a loss in intensity of all bands is observed (spectrum (b)).

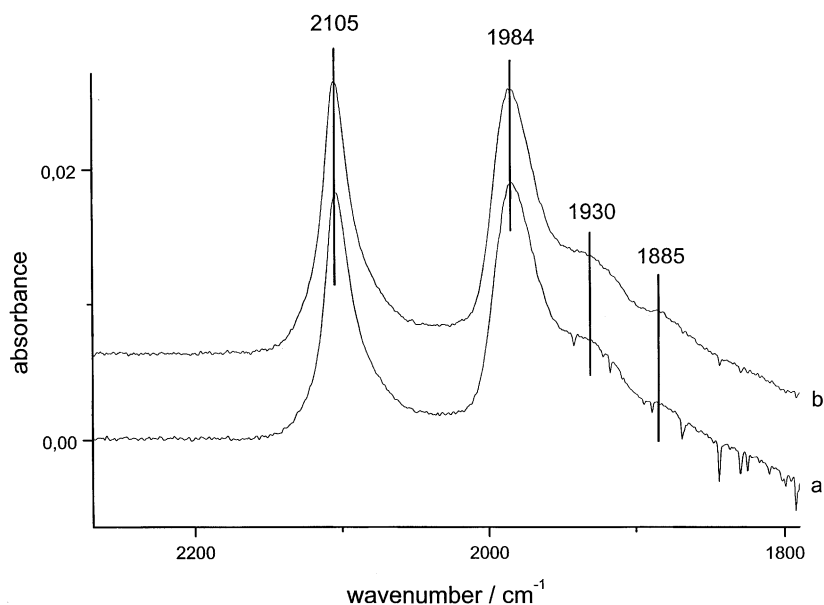


Fig. 2. IR spectra of adsorbed CO after pretreatment under CO (570 K): (a) at RT under 1 hPa CO; (b) at RT under 10 hPa CO.

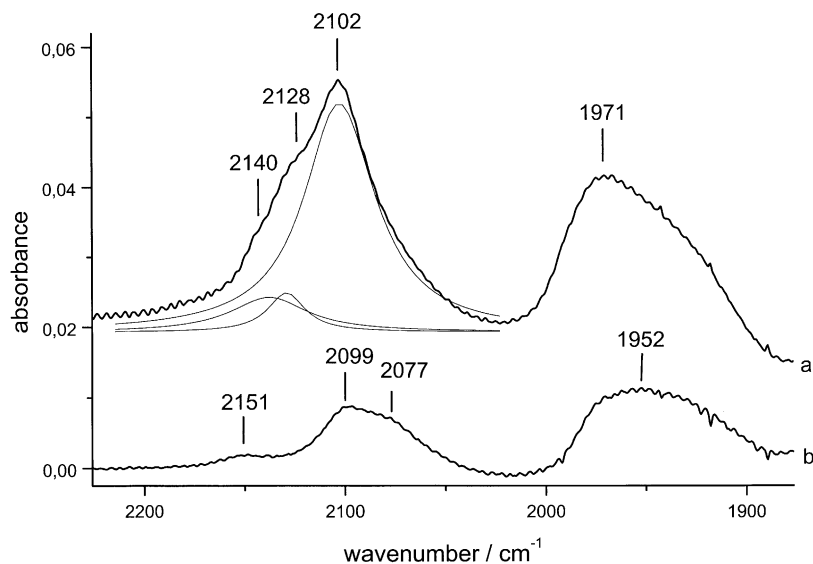


Fig. 3. IR spectra of adsorbed CO after pretreatment under N_2 (570 K): (a) at RT under 100 hPa CO; (b) after vacuum treatment (RT, 15 min). The narrower lines shown under spectrum (a) indicate the results of peak de-convolution.

The maximum for the broad, low frequency band has now shifted to 1952 cm^{-1} , indicating a predominance of isolated bridging carbonyls at the lower surface coverages. In the monocarbonyl region, a maximum of 2099 cm^{-1} is now observed (Pd^0 -CO). The shoul-

der at 2077 cm^{-1} is also attributed to Pd^0 -CO, though the difference in wavenumber indicates a highly non-homogeneous distribution of metal sites. A weak band at 2151 cm^{-1} which is assigned to adsorption on Pd^{2+} sites is now also observable, though no band for

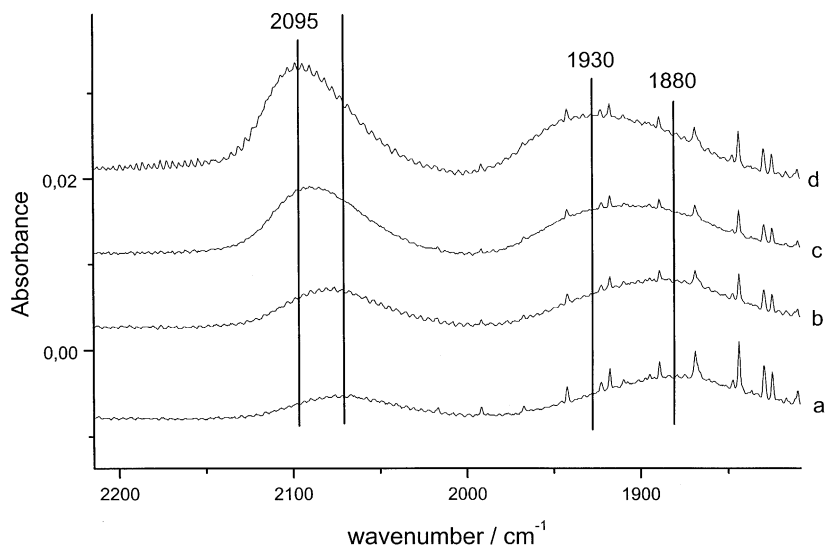
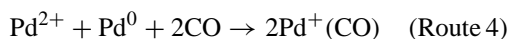


Fig. 4. IR spectra of adsorbed CO after pretreatment under static vacuum (570 K): (a) under 0.1 hPa CO; (b) 0.5 hPa CO; (c) 10 hPa CO; (d) 50 hPa CO.

$\text{Pd}^+ \text{-CO}$ species is detected. This can be explained by a possible vacuum-promoted disproportional reaction (Route 4), which generates Pd^{2+} and Pd^0 sites [18,19]:



3.5. Pretreatment under static vacuum

Pretreatment of the $\text{Pd}(\text{acac})_2/\text{SiO}_2$ sample under static vacuum, without additional oxidation or reduction steps, generates a surface on which only Pd metal is detected via CO adsorption. On admission of 0.1 hPa CO two broad bands with maxima at ca. 2070 and 1880 cm^{-1} are observed (Fig. 4, spectrum (a)). The former is assigned to the monocarbonyl species, and the latter to the triply bridged species, $(\text{Pd}^0)_3\text{-CO}$ [11,13]. With increasing CO pressure both bands gain in intensity and the maxima shift to higher wavenumbers, until upon reaching saturation under 50 hPa CO (spectrum (d)), values of 2095 and 1930 cm^{-1} are achieved. This is a reflection of the increasing CO coverage on the surface, resulting in conversion of triply bridging carbonyls (three-fold coordination) to isolated, bridging carbonyls (two-fold coordination), and a greater influence of dipole-dipole interactions from neighbouring monocarbonyls.

4. Discussion

Previous studies concerning the generation of supported Pd particles from $\text{Pd}(\text{acac})_2$ have involved decomposition of the precursor under O_2 (usually at 673 K), followed by reduction of the evolved PdO to Pd metal under H_2 (473–773 K) [3,13]. Attempts to decompose the complex under non-oxidising conditions resulted in the formation of a carbonaceous residue, which partially covered the Pd sites and thus decreased the catalytic activity [1].

In this study we have performed the decomposition of the $\text{Pd}(\text{acac})_2$ precursor under five different atmospheres, and have investigated the nature (in terms of oxidation state and degree of aggregation) of the generated Pd surface species in each case, through controlled admission of CO probe molecules. In addition to pretreatment under O_2 and H_2 , in order to confirm previously reported observations, the decomposition

of the $\text{Pd}(\text{acac})_2$ precursor was attempted under CO and N_2 flow, as well as under static vacuum.

Under oxidising conditions, Pd^{2+} species (most likely PdO particles) were generated which could then be readily reduced under a static atmosphere of CO. A point of interest, however, was the presence of metallic Pd in this oxidised sample immediately upon admission of CO. A possible explanation for this is the reduction of PdO by CO (or other reducing fragments) released during the decomposition of the acac ligands (see Routes 2 and 3). All traces of Pd in higher oxidation state were removed via reduction with CO, and only linear and bridged carbonyl species bound to the metal were subsequently detected (Fig. 1). Similar spectra were recorded after direct reduction of the precursor under CO, which indicated that a surface containing only Pd^0 could actually be attained with a one-step pretreatment procedure (Fig. 2). Indeed, the intensity ratio of linear carbonyl to bridging carbonyl species in this sample indicated that smaller Pd particles had been generated than in the previous two-step process. However, the reverse is true when one compares these spectra with that for the oxidised sample after a second oxidation–reduction cycle (Fig. 1, spectrum (e)). It now becomes apparent that direct reduction of the complex using CO, though generating metallic Pd on the silica surface, fails to fully remove the organic residue derived from the decomposition of the ligands. This, it would appear, is only removed after prolonged oxidation. Indeed, not only does a second oxidation–reduction cycle clear the surface of organic debris and expose more Pd, but appears to actually enhance the dispersion of the Pd particles as well.

Strongly reducing (H_2 flow) conditions, on the other hand, caused the organic ligands to decompose and form a carbonaceous deposit over the support surface, which blocked the Pd sites and prevented their interaction with the CO probe molecules. Attempts at removing the deposit through further reduction resulted in the formation of a carbide-like layer over the surface, which continued to block the Pd centres to CO adsorption.

Under inert conditions pretreatment led to the formation of a combination of Pd^{2+} , Pd^+ and Pd^0 centres. It would appear, therefore, that the decomposition of the ligands under N_2 with the ensuing release of reducing components, partially brought

about the reduction of PdO to Pd metal. One factor to consider here is that the pretreatment was carried out under flow conditions. Hence, it is possible that the evolved reducing components, most likely CO (Route 2), were carried away from the sample without the chance of adsorbing onto Pd²⁺ sites and carrying out the reduction (Route 3). Even after vacuum treatment, which led to the removal of the Pd⁺-CO species, Pd²⁺ sites were still detected. The broad linear carbonyl and bridging carbonyl bands also suggested a non-homogeneous dispersion of the generated Pd⁰ sites, possibly due to the presence of agglomerated particles containing mixed valence Pd, or due to partial coverage of the surface through unremoved organic residue.

The selective generation of Pd⁰ sites was successfully achieved, however, through thermal treatment of the Pd complex under static vacuum. Though the exact decomposition mechanism was not investigated, it seems that the static conditions enabled the released reductants to re-adsorb onto the surface and ensure the complete reduction of all Pd species. The presence of a broad band assigned to the Pd⁰-CO monocarbonyl species, however, does once again infer a rather non-homogeneous dispersion of Pd metal particles, though the lack of compressed bridging carbonyls suggests that at least the particle size is relatively small. Hence, it is possible to generate Pd particles on a silica support via a one-step decomposition of the Pd(acac)₂ precursor, though in this present study we did not quantitatively ascertain the amount of Pd exposed, or indeed the amount of unburnt organic material left on the surface, and its influence on any catalytic reactions.

5. Conclusions

The decomposition of the Pd(acac)₂ precursor complex was attempted under five different pretreatment atmospheres, though the oxidation state and degree of dispersion of the resulting Pd species depended heavily on the conditions employed. In two cases, under CO flow and static vacuum, selective one-step generation of dispersed Pd metal was achieved, though it was not known to what extent the complex had been reduced

or indeed to what degree the Pd was exposed. Furthermore, the presence of metallic Pd after pretreatment under O₂, N₂ and vacuum supports the case that decomposition of the Pd(acac)₂ precursor proceeds via the release of reducing fragments.

Acknowledgements

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