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ORIGINAL PAPER

A Comparison of Experimental Procedures for the Application of Infrared Spectroscopy to Probe the Surface Morphology of an Alumina-Supported Palladium Catalyst

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Abstract

Structure/function relationships in heterogeneous catalysis play an important role in catalyst design strategies. The combination of chemisorption of suitable probe molecules alongside application of infrared spectroscopy is an established technique for providing information on the metal crystallite morphology of supported metal catalysts. Following a review of key literature on this topic, a variety of experimental arrangements that may be adopted for this task are examined. Specifically, the adsorption of CO over a 5wt% Pd/Al_2O_3 catalyst is investigated using transmission and diffuse reflectance sampling options and two research grade spectrometers. Although comparable spectra are obtained on all the platforms examined, differences are noted. In particular, temperature-programmed IR spectroscopy on one platform enables resolution of two features assigned to linear CO bound to the Pd particles. The relevance of this sub-division of terminal sites with respect to selective hydrogenation reactions is briefly considered.

Keywords Infrared spectroscopy · CO chemisorption · Alumina-supported palladium catalyst · Diffuse reflectance · Transmission

1 Introduction

Infrared (IR) spectroscopy provides a platform for the observation of interactions between adsorbates and surfaces; thus, it plays a pivotal role in the characterisation of heterogeneous catalysts [1]. Heterogeneous catalysts are typically designed such that they provide well-dispersed active sites distributed on the catalyst surface, maximising interactions between reactants and said active sites. The ease of performing in situ Fourier transform infrared (FT-IR) studies during catalysis makes FT-IR spectroscopy an ideal candidate for the identification of active sites in catalysts [2].

Correlation between catalyst activity and the characterisation of active sites is essential for a full understanding of chemical processes and catalyst optimisation [3]. Surface active sites of metals of heterogeneous catalysts exist in various geometries and are typically characterised by their location on the metal surface, *e.g.* plane, corner, edge. Surface sensitive reactions infer the existence of varying activation barriers for reactions on different active site geometries [3]. For example, Couto et al. investigated the effect of metal particle size for two 0.3wt% Pd/Al_2O_3 catalysts for nitrobenzene hydrogenation [4]. One catalyst with particle sizes in the range of 1.2–2.5 nm exhibited by-product formation of *ca.* 5×10^3 ppm after 175 min on stream. Comparatively, another catalyst with a particle size distribution in the range of 4.0–6.0 nm gave *ca.* 1×10^3 ppm of secondary products. Thus, the effects of differing particle size, and so differing geometric active sites, can have a direct effect on catalyst activity. These concepts are encompassed within the domain of *structure sensitive* reactions [5].

The incident radiation utilised in FT-IR spectroscopy can interact with a sample in a multitude of ways: the light may be absorbed, specularly (singly) reflected or diffusely (multiply) scattered by a surface [6]. Diffuse reflection infrared

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Fourier transform spectroscopy (DRIFTS) is the process in which radiation penetrates a sample and is subsequently scattered by individual particles throughout the sample matrix. As the IR beam penetrates the sample, it is possible to obtain information regarding the material's characteristics by consideration of absorbed radiation [7]. Additionally, the scattering of incident radiation provides DRIFTS set-ups with a large equivalent path length compared to those observed during transmission infrared (TIR) measurements, overcoming the low optical efficiency associated with diffusely reflected radiation [8]. As diffuse reflection spectra are obtained via an absorption process, they bear similarities to spectra obtained via TIR measurements, i.e. both present absorption bands. A further consideration linked to using IR to probe dense 2-dimensional networks such as adsorbed overlayers is the matter of dipole coupling, where intensity transfer must be considered during spectral interpretation [9]. The degree of dipole–dipole interactions relies on the distribution of similar atoms on neighbouring sites. Thus, as surface coverage on a catalyst changes, peak shifts and modification of band intensity is probable and can significantly complicate the inference of populations at higher coverages.

This article is rooted in using IR spectroscopy to assess metal crystallite morphology of supported metal catalysts applied to selective hydrogenation reactions [10–12], where there is an interest to consider how hydrogen may partition at a metal surface. The following sections of the Introduction will firstly consider how certain metal sites may be linked to hydrogenation activity. Secondly, it will provide a brief overview of how CO can be used as a probe molecule to characterise those active sites. The Results and Discussion section will then make comparisons between TIR and DRIFTS spectra of chemisorbed CO over a representative hydrogenation catalyst.

Basset et al. utilised IR spectroscopy to investigate adsorption of reversibly and irreversibly bound hydrogen on Pt/Al_2O_3 [13]. Adsorption of solely irreversibly bound hydrogen yielded no hydrogenation of benzene, indicating that only reversibly bound hydrogen was involved in catalytic activity. Reversibly bound hydrogen is IR active and gives a band centred at *ca.* 2120 cm^{-1}; irreversibly bound hydrogen on Pt/Al_2O_3 is not discernible via IR spectroscopy [14]. It was also found that the IR signal corresponding to the weakly bound hydrogen and catalytic activity were both pressure dependent, furthering the argument that it was indeed weakly bound hydrogen which was responsible for benzene hydrogenation [13]. Although Basset et al. did not assign a specific site for hydrogen binding, they were able to associate active hydrogen adsorption on Pt/Al_2O_3 with the Pt-H band at *ca.* 2120 cm^{-1}. Primet et al. have considered the effects symmetry factors have on IR spectra of weakly adsorbed hydrogen, and state that as only one IR band is observed for reversibly bound hydrogen on Pt/Al_2O_3, it is likely that each hydrogen atom is bonded on-top of a single Pt atom [15]. A $Pt(H)_2$ species would be expected to give two IR bands. Thus, it appears that the hydrogen responsible for hydrogenation activity on platinum catalysts is adsorbed onto on-top sites. Linking into these concepts, a proton NMR investigation into hydrogen adsorption on Pt/SiO_2 also states that weakly bound hydrogen adsorption occurs on the on-top Pt sites [16]. Collectively, these investigations present a convincing argument for adsorption of active hydrogen to on-top sites for Pt catalysts, i.e. these sites are implicated in contributing to hydrogen supply for metal catalysed selective hydrogenation reactions.

Palladium finds wide application in selective hydrogenation reactions. Morkel et al. have examined the interaction of hydrogen on a Pd(111) single crystal and Pd/Al_2O_3 catalyst using sum frequency generation vibrational spectroscopy and thermal desorption spectroscopy [17]. It was found that Pd nanoparticles permitted the formation of Pd-H at lower hydrogen exposures than the Pd(111) single crystal, and so it was suggested that the edge, corner, step and defect sites present in the Pd/Al_2O_3 catalyst facilitated hydrogen supply for hydride formation—i.e. minority sites on the catalyst expedited hydrogen supply. More recently, an investigation into the effects of various catalyst parameters on the formation of palladium hydride (PdH) in commercial Pd hydrogenation catalysts, revealed the first observation of hydrogen adsorbed on the on-top site of β-PdH via inelastic neutron scattering (INS) [18]. A previous study by Borodzinksi et al. found the β-PdH phase had higher activity and selectivity for ethyne hydrogenation to ethene than the α-PdH phase [19]. Thus, it is possible that it may be hydrogen adsorbed on top of β-PdH that gave this increased catalytic activity.

Whilst the relevance of site-selective chemistry within certain metal-catalysed hydrogenation reactions is noted, it is a non-trivial matter to use IR spectroscopy of chemisorbed hydrogen to discern passive and active adsorption sites. However, FT-IR studies of CO adsorption over, for example, supported Pd catalysts has a role for defining active site distributions, which can then be correlated with observed reaction trends [10–12]. Against this background, it is informative to consider milestones in the use of IR techniques combined with CO chemisorption to discern the active site distribution of supported metal catalysts. The article concentrates on the application of TIR and diffuse-reflectance techniques.

Previously, TIR measurements were more popular than DRIFTS, owing to the technique's sensitivity for weakly IR absorbing species and a comparatively simplistic set-up [20]. However, TIR measurements require preparation of a thin disc of sample which may lead to structural changes from mechanical pressure, limiting the practicability of TIR for discerning catalyst active sites. Moreover, the preparation of suitably transmitting discs of sufficient mechanical strength for manipulation can be a challenging exercise [20]. In contrast, DRIFTS is well suited to analysing fine powders, as may routinely be encountered with heterogeneous catalysts. Also, fine powders facilitate efficient gas exchange, providing the possibility of the DRIFTS cell being linked to in-line analytics such as mass spectrometry [21]. These attributes present an argument for the superiority of DRIFTS for in situ measurements of catalysts. However, one must not disregard or underestimate the useful information obtained via TIR when interpreting DRIFTS spectra or overlook the effect a chosen IR technique may have on collected spectra. This point was effectively demonstrated by Holmes et al. who investigated the variations in collected spectra of CO chemisorption on a Pt/SiO_2 catalyst, EUROPT-1, via TIR and DRIFTS [20]. The spectra were collected on the same spectrometer, permitting a direct comparison of the two techniques on spectral output. Both spectra exhibit similar absorption bands, but the relative intensities of those bands varied within the two set-ups. Above 2200 cm^{-1}, larger absorbance was reported for the DRIFTS spectrum owing to the increased path length through the catalyst arising from the diffuse scattering of light. However, below this threshold, specular or diffuse specular reflection from the silica support resulted in a reduction in absorption and, in turn, the TIR spectrum exhibited the largest absorption below 2200 cm^{-1}. Holmes et al. also presented a spectrum post-ethene exposure to EUROPT-1, acquired via a DRIFTS set-up, and compared this to a post-ethene exposure spectrum acquired via a TIR set-up from a previous study. Both techniques provided comparable sensitivity. However, the spectrum collected via TIR presented useful information at a lower wavelength than DRIFTS: down to 1300 cm^{-1} compared to 1400 cm^{-1} for the DRIFTS measurement. Thus, Holmes et al. highlight the importance of understanding the effect the IR technique utilised may have on spectral acquisition. Elaborating on these issues, Sirita et al. have considered the difficulty of reproducing packing in some commercial DRIFTS cells [22]. Upon emptying, re-loading and repeat DRIFTS measurements, a noticeable variation in intensity values was observed, illustrating that care must be taken to ensure consistent cell packing is achieved.

The popularity of DRIFTS as an investigative technique for heterogeneous catalysts has recently flourished and is owed to the ease of in situ measurements and availability of a selection of affordable commercial cells [23]. To investigate the true nature of active sites on a catalyst it is essential for reaction conditions to be maintained [22]. A common application of DRIFTS in heterogeneous catalysis is for surface characterisation [23]. The surface coverage of an adsorbing species, for example CO, is followed via IR spectroscopy as a function of increasing temperature. Moreover, it can be used to discriminate between different species and sites, unlike other methods employed for absolute determination of heat of adsorption, such as calorimetry. Informative examples on the application of DRIFTS to characterise supported metal catalysts are considered below.

An example of site discrimination of the metal crystallites of supported metal catalysts is provided by Bianchi et al. who reported heats of adsorption of CO on a variety of Pd/Al_2O_3 catalysts under isobaric conditions (1% CO/He) via adsorption equilibrium infrared (AEIR) spectroscopy [24, 25]. FT-IR spectra of CO adsorbed on a 2wt% Pd/Al_2O_3 catalyst are presented at varying temperatures [24], proposing two linear (on-top) adsorption sites with differing heats of adsorption and two bridging adsorption sites with similar heats of adsorption. Interestingly, all four sites are not observed simultaneously in this study. At room temperature only one linear CO band is observed and is associated with weakly bound linear CO. With increasing temperature, the intensity of this band decreases and shifts to lower wavenumbers until a temperature of *ca.* 580 K is reached, after which no further shift in wavenumber was observed. The observed change in wavenumber with increasing temperature was attributed to the loss of weakly bound linear CO which revealed a small amount of strongly adsorbed linear CO at higher temperatures, which was previously masked in IR spectra by the weakly adsorbed linear species. For the bridging CO species, two individual bands were observed at room temperature; however, with increasing temperature the higher wavenumber band was observed to shift until both bands merged at *ca.* 430 K. Very similar trends were reported in earlier work by Bianchi et al. concerning CO adsorption on 1.4wt% Pd/Al_2O_3 [25]. These studies highlight the importance of temperature-programmed infrared spectroscopy (TP-IR).

In this communication, we compare the difference in spectral acquisition of adsorbed CO over a Pd/Al_2O_3 catalyst using TIR and DRIFTS. The performance of two separate research grade spectrometers and certain commercially available sample cells will be addressed to discern the effect different sample environments and instrumentation have on spectral output. The Pd/Al_2O_3 catalyst represents a generic Pd based selective hydrogenation catalyst. The relevance of the resulting morphological deductions with respect to sites effecting hydrogen supply in selective hydrogenation reactions will be briefly considered.

2 Experimental

2.1 Catalyst and Infrared Instrumentation

A Pd/Al_2O_3 (5wt% on γ alumina powder) catalyst was obtained from Alfa Aesar (cat. ref.: 11713, surface area: 140 ± 10 m^2g^{-1}) [26]. The use of a single catalyst sample enabled comparisons to be made between different spectrometer/sample environment accessories. Spectra are presented as difference spectra, where the spectrum of a clean, activated catalyst has been subtracted from that of a CO dosed spectrum. "Absorbance" is utilised for y-axes titles in presented IR spectra for briefness, however all DRIFTS spectra are strictly given in terms of 'pseudo-absorbance' as described by Sirita et al. [22].

2.1.1 Transmission FT-IR

For TIR measurements a self-supporting disc was prepared. *ca.* 20 mg of catalyst was ground into a fine powder and placed into a pellet dye (Diameter: 13 mm, Graseby Specac) between sheets of mica (Attwater Group). The dye was placed into a press (Perkin Elmer 15.000) and evacuated via rotary pump. Pressure (0.5–1.75 tons cm^{-1}) was applied for 10 min. In situ IR experiments were performed using a Bruker Vertex 70 spectrometer equipped with a high D* MCT detector. The disc was contained within a Harrick High Temperature Cell.

2.1.2 DRIFTS

DRIFTS analysis used a typical sample size of *ca.* 50 mg of as-received catalyst. In situ IR measurements were performed using two separate FT-IR spectrometers: (i) a Bruker Vertex 70, equipped with a Harrick Praying Mantis diffuse reflectance cell with high temperature reaction chamber, and (ii) a Nicolet Nexus FT-IR spectrometer fitted with a SpectraTech Smart diffuse reflectance cell and environmental chamber. Similarly, the Nexus spectrometer is operated with a high D* MCT detector.

Figure 1 presents schematic diagrams of the optical design for (a) the SpectraTech Smart diffuse reflectance cell and (b) the Harrick Praying Mantis cell with high temperature reaction chamber. It is immediately apparent that both DRIFTS cells exhibit different optical designs, and that the optical path length of IR radiation from the light source to the detector within the spectrometer is greater for the Harrick set-up (b). The distance from the sample to the first optical element is also critical. Equation 1 relates the effect of distance on light intensity [27].

$$I \propto \frac{1}{r^2} \tag{1}$$

where I is light intensity and r is the distance from the light source. Light intensity decreases with increasing distance. Thus, it follows that one would anticipate the SpectraTech (a) cell to be associated with a greater sensitivity for IR measurements than the Harrick (b), due to its shorter optical pathlength permitting a lower degree of lost light intensity.

Different spectrometers are used with both DRIFTS cells. This is a consequence of the SpectraTech smart diffuse reflectance cell being integrated within the Nexus spectrometer. Thus, a direct comparison of cell efficiency in this study is not possible. Instead, overall "set-ups" of both spectrometer and DRIFTS cell are compared. Furthermore, it is worthwhile noting that the two DRIFTS arrangements under consideration offer different reactor attributes, which may influence the selection of a particular cell for a specified reaction. For example, although the optical arrangement is seemingly more elaborate in the case of the Harrick design, the actual reactor is distinct from the focussing elements, meaning corrosive reagents/products will not affect optical throughput. However, whilst the relative simplicity of the SpectraTech design facilitates efficient optical throughput, as the collection optics are within the environmental cell, the gold coated optical element (M2) is potentially vulnerable to corrosive reagents/products. Progressive corrosion of this optical element could lead to changes in optical throughput. Thus, the selection for which diffuse accessory is best suited to interrogate a particular adsorbate/substrate system, or indeed reaction system, may depend on the physico-chemical characteristics of the individual reaction system.

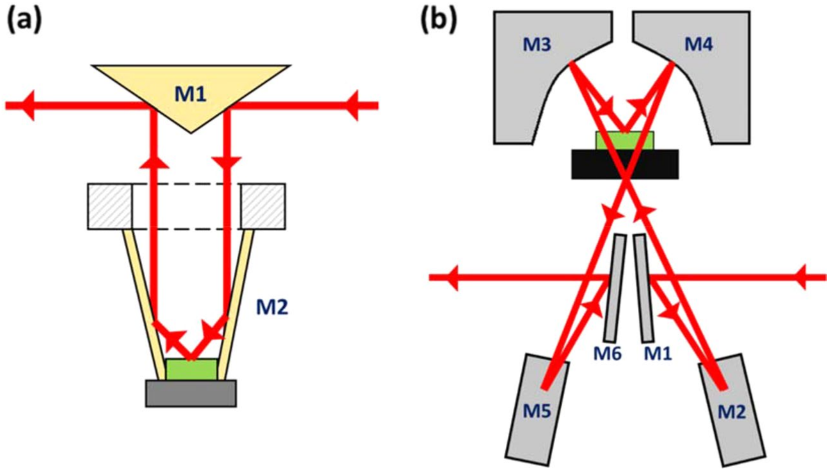

Fig. 1 Schematic representation of (**a**) the SpectraTech Smart diffuse reflectance cell with Nexus Smart collector [39] and (**b**) the Harrick Praying Mantis diffuse reflectance cell with high temperature reaction chamber [40]. The optical design schematics are adapted from the given references. Mx signifies the positioning of optical elements in each cell. The catalyst sample is shaded in green

2.2 Temperature Programmed IR Measurements

Both spectrometers are connected to individual gas manifolds that provide control of gas flow into the infrared cell. For temperature-programmed IR (TP-IR) measurements, the same procedure was followed for the Bruker and Nicolet set-ups. The as-received catalyst was reduced in a flow of He (BOC gases, 99.9%) and H_2 (BOC gases, 99.8%) while heated to 383 K and held at this temperature for 30 min. The temperature was increased to 473 K for 1 h, with H_2 flow stopped after 30 min. The cell temperature was reduced, and a background spectrum recorded at 303 K. The sample was exposed to pure CO (CK gases, 99.99%) via a custom-built glass line and subsequently flushed with He to remove non-chemisorbed CO from the chamber. Spectra were recorded at 303 K for 512 scans (4 cm^{-1} resolution). For desorption experiments, the catalyst was heated in situ under He flow and maintained at the designated temperature for 10 min before cooling to 303 K for spectral acquisition. This process was repeated for 323, 373, 423, 473, 523, and 573 K. Presented spectra are background subtracted with no other signal treatment performed.

3 Results

3.1 CO Chemisorption

Before embarking on temperature-programmed measurements, the CO adsorption isotherm was measured to gauge the saturation level of the Pd/Al_2O_3 catalyst. A custom-built glass vacuum line with an on-line gas chromatograph (Thermo Finnigan, Trace GC) was utilised to pulse known volumes of CO across the as-received sample [28]. The saturation level was measured to be 95.80 µmol CO $g^{-1}_{(cat)}$. Concentration of surface palladium atoms can be determined assuming a surface stoichiometry of CO:Pd = 1:2 [29], that estimate the particle size to be 2.7 nm with a metal dispersion of 41%.

3.2 Comparing TIR vs. DRIFTS on Bruker Vertex Spectrometer

A direct comparison between transmission and DRIFTS set-ups was undertaken using the Bruker Vertex 70 spectrometer. Figure 2a presents the TIR series of spectra, whilst the equivalent DRIFTS spectra are presented in Fig. 2b. CO adsorption spectra are obtained at room temperature (303 K) and, thereafter, spectra are obtained after heating the sample to selected temperatures (323–573 K) that induce desorption of CO from the catalyst surface. The spectra obtained on warming therefore provide an indication of the enthalpy of adsorption of CO on the accessible Pd adsorption sites [19]. In both cases (Fig. 2a, b) the room temperature spectra show 3 distinct features that are assigned as follows: a weak band at *ca*. 2060 cm^{-1} associated with linearly bound CO, an intense band at *ca*. 1980 cm^{-1} corresponding to bridge bonded (μ_2) CO on a Pd(100) plane and a band at *ca*. 1910 cm^{-1} arising from bridge bonded (μ_3 hollow) CO on a Pd(111) plane [10]. A similar peak profile for bridging CO species on Pd/MgO was observed by Bertarione et al.; that is a sharp, high intensity (μ_2) CO feature and a broad (μ_3) CO feature [30]. Bertarione and co-workers attributed the appearance of the (μ_2) CO band to CO adsorption onto highly regular polycrystalline faces, corroborated by TEM images. Moreover, the broadness of the band associated with (μ_3) CO adsorption indicated a high heterogeneity of adsorption sites.

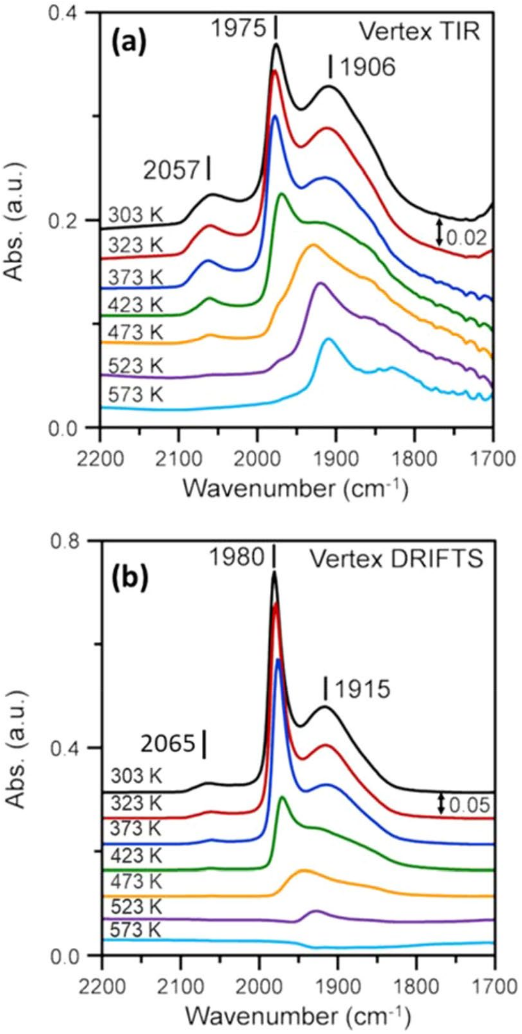

Fig. 2 In situ TIR (**a**) and DRIFTS (**b**) of temperature programmed CO desorption using the Bruker Vertex spectrometer. The spectra are respectively scaled vertically by 0.02 and 0.05 a.u. to facilitate observation

Differences in absorbance values for the 303 K spectra are readily identifiable between both techniques, with the bridge bonded (μ_2) CO feature more prominent in the DRIFTS set up (Fig. 2b). This may be a result of the larger optical path length experienced during DRIFTS measurements due to diffusely scattered light. However, the overall peak profile and distribution is consistent across both measurement set-ups. Upon increasing the desorption temperature, the intensity of all features decreased independent of the measurement set-up. In the transmission cell, linearly bound CO was present at 473 K, with linear CO fully desorbing somewhere in the range of 473–523 K (Fig. 2a). A population of bridge bonded (μ_2) and (μ_3) CO remain at 573 K but are severely diminished. An additional weak shoulder was observed at *ca.* 1980 cm^{-1} for desorption temperatures of 473 and 523 K in the TIR spectra. This feature is likely a result of some defect site on the 5wt% Pd/Al_2O_3 catalyst. This is a reasonable assumption, as a high level of defects are typically observed for alumina supported Pd catalysts [30].

For the DRIFTS set-up (Fig. 2b), reduction in absorbance on increasing temperature was more apparent. Linearly adsorbed CO was only observed up to 423 K and was absent at higher temperatures. Interestingly, after heating to 523 K only a band corresponding to (μ_2) CO was observed, suggesting that the more highly coordinated (μ_3) CO is lost before (μ_2) bonded CO. Comparison with the TIR spectra show this to not be the case and highlights the significance and benefit of having reference to TIR spectra of a chemisorbed species when interpreting DRIFTS, as previously discussed by Holmes et al. [20]. In contrast to the TIR measurement (Fig. 2a), Fig. 2b shows the absence of bridging CO species at 573 K. Instead, this spectrum exhibits weak negative IR features between 1900 and 1850 cm^{-1} suggesting that the reference spectrum (activated catalyst) used for background subtraction did not represent a stable Pd/Al_2O_3 catalyst free of adsorbates. Utilisation of the activated catalyst as a reference spectrum for background subtraction during CO chemisorption IR measurements is common practice [31, 32], however it is noted that use of a clean KBr spectrum for background subtraction [33] would avoid the matter of weak negative features in difference spectra.

Additionally, the effects of dipole coupling on linear and bridging (μ_2) and (μ_3) CO in spectra collected via the different set-ups has been considered. Linearly adsorbed CO species did not exhibit any shift in wavenumber with varying desorption temperature. This is characteristic of a single species decoupled from any neighbouring adsorbates and suggests linear CO adsorption occurs on low coordinated Pd sites such as corners and edges [10]; minority sites which may be directly involved in hydrogen supply on the catalyst [10, 15, 17]. As the linear CO feature desorption was complete at the lowest temperatures, this indicates this moiety to possess the lowest enthalpy of adsorption of the three principal surface species.

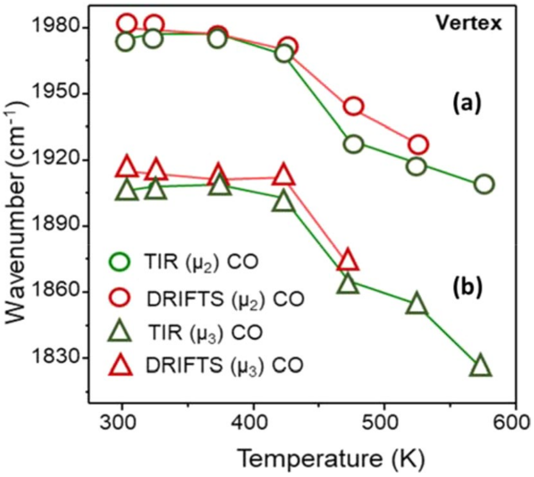

Fig. 3 Variation in the wavenumber values for (**a**) (μ_2) and (**b**) (μ_3) bound CO upon increasing temperature using the Bruker Vertex spectrometer

Table 1 The shift in wavenumber over low and high temperature ranges observed for TIR (Harrick) and DRIFTS (Harrick) set-ups on the Bruker Vertex spectrometer

IR technique	Temperature (K)	Wavenumber shift ($cm^{-1}K^{-1}$)	
		μ_2	μ_3
TIR	< 423	0.06	0.02
	> 423	0.4	0.5
DRIFTS	< 423	0.08	0.02
	> 423	0.4	0.8

Peaks arising from bridging CO demonstrated not only a decrease in absorbance values with increasing desorption temperature but also a distinct decrease in wavenumber. This observed frequency decrease is indicative of reduced dipole coupling effects as the population of adsorbed CO is reduced. Figure 3 presents the shift in wavenumber for bridging (μ_2) and (μ_3) CO as a function of desorption temperature. Both set-ups observe the same pattern regarding wavenumber shift, a decrease in wavenumber with increasing temperature. This suggests that physical parameters, such as differing heating set-ups, or gas residence times arising from the different geometries of the sampling environments, are not affecting spectral acquisition and spectral trends from both techniques are comparable [7].

Further consideration of Fig. 3 revealed two different rates of wavenumber shift of bridging CO modes for spectra collected below and above 423 K. Table 1 gives wavenumber shift as a function of temperature observed for each set-up in the stated temperature ranges. In both set-ups, bridging (μ_2) and (μ_3) CO appeared to desorb very slowly for desorption temperatures in the range of 303–423 K and, in turn, both bridging CO species exhibit a very small shift in wavenumber. Desorption temperatures greater than 423 K resulted in an increased desorption of bridging CO species and a significant shift in wavenumber to lower values. From Fig. 3 it is evident that both bridging species desorbed at similar temperatures and at similar rates. Thus, both bridging CO species have similar desorption temperatures, as observed previously [24, 25].

It is noted that the cells associated with TIR and DRIFTS measurements utilise different heating arrangements, so differences in heating capabilities of the cells could potentially compromise uniformity of spectral outcomes during thermal ramping experiments. Li et al. highlight the discrepancies that can arise between thermocouple bed readings and the temperature of the catalyst as measured by optical pyrometry [34]. Thus, it is possible that discrepancies in actual catalyst temperatures within the TIR and DRIFTS cells examined could contribute to the CO desorption differences observed in Fig. 2. The use of temperature calibration curves as outlined by Li et al. [34] is a useful practice to gauge this possibility. However, the close coincidence of wavenumber shift with temperature (Fig. 3; Table 1) for the TIR and DRIFTS measurements undertaken using the Vertex spectrometer indicate comparable sample temperatures are experienced in both cases within the 300–573 K range studied here.

Dipole coupling effects are greatest for large populations of chemisorbed species, due to increased lateral interactions between neighbouring adsorbates [9]. Accordingly, the true singleton frequency of an adsorbed species will be observed for lower surface coverages, with lesser dipole coupling effects. Therefore, the singleton frequency values for bridging CO species presented in this investigation will be those observed at the highest desorption temperature values. The singleton frequencies for bridging CO on the Bruker Vertex spectrometer are as follows: (μ_2) CO is 1909 cm^{-1} and (μ_3) CO is 1826 cm^{-1} for TIR, and (μ_2) CO is 1928 cm^{-1} and (μ_3) CO is 1872 cm^{-1} for DRIFTS. The differences in wavenumber when comparing different IR techniques is anticipated [35].

Although it should be highlighted that the sampling environments of the transmission and DRIFTS set-ups used different sample masses in this instance (*ca.* 2.5 times greater in the case of the DRIFTS measurement), the clear discrepancies in the absorbance profiles with temperature observed in Fig. 2 exemplifies the set-up dependent variables that must be considered when performing IR measurements.

3.3 DRIFTS Comparison on Nicolet Spectrometer

A comparative DRIFTS measurement was performed using a Nicolet Nexus spectrometer/SpectraTech smart diffuse reflectance accessory to assess deviation in the observed trends from the Bruker Vertex/Harrick transmission cell/Harrick diffuse reflectance accessory. Figure 4 presents collected spectra for the CO desorption study with the Nicolet Nexus spectrometer/SpectraTech smart diffuse reflectance accessory. The various CO bound states observed in Fig. 2 are also present here and follow a similar absorbance profile as previously observed. However, the linearly bound CO feature is resolved to a central peak at 2057 cm^{-1}, with a noticeable shoulder at 2076 cm^{-1}. These two bands correspond to CO adsorbed linearly on two different geometrical Pd sites, edge and corner, sites which are thought to be linked to hydrogen supply for hydrogenation [10, 17]. CO adsorption to the latter is responsible for the appearance of the shoulder at 2076 cm^{-1} and adsorption to edge sites gives the band at 2057 cm^{-1} [10]. The distinction between linear CO adsorption on corner and edge sites is apparent until 423 K when the peak shoulder feature was lost due to full desorption of CO adsorbed linearly on corner sites. Comparatively, linear CO present on edge sites was observable after heating to 523 K. This indicates that the two types of linearly adsorbed CO (corner and edge) have different desorption temperatures. This result is consistent with reports of CO chemisorption on Pd by Bianchi et al. [16, 17] and Lear et al. [10]. Bridge bonded (μ_2) and (μ_3) CO was observable after heating to 573 K which contrasts with the DRIFTS spectra

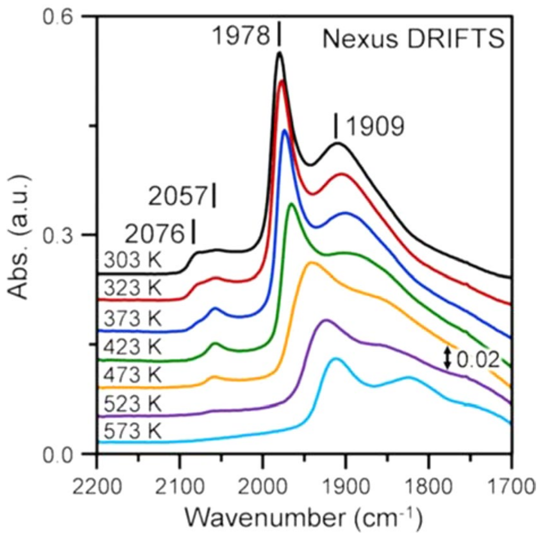

Fig. 4 In situ DRIFTS spectra of temperature programmed CO desorption using the Nexus spectrometer/SpectraTech smart diffuse reflectance accessory. The spectra are scaled vertically by 0.02 a.u. to facilitate observation

collected with the Bruker Vertex (Harrick), where no bridge bonded CO was observed after heating to 573 K.

The frequency shift of all bands exhibits the same general pattern as those observed for the DRIFTS measurement performed with the Bruker Vertex (Fig. 3); whilst bridge-bonded CO bands shift to lower wavenumber as these states are depopulated, the frequency of the on-top site is invariant. Figure 5 presents the variation in wavenumber for the (μ_2) and (μ_3) CO band as a function of temperature collected via DRIFTS on the Nicolet Nexus spectrometer/SpectraTech smart diffuse reflectance accessory. As with the results obtained from the Bruker spectrometer, Table 2 shows two different rates of wavenumber shift for spectra collected below and above 423 K. Again, a small shift in the frequency of bands corresponding to (μ_2) and (μ_3) bridging CO species in the temperature range of 303–423 K suggests a slow rate of desorption of bridging CO species from the Pd/Al_2O_3 catalyst. Above 423 K the rate of bridging CO desorption increased, enhancing the effects of dipole coupling on collected spectra and giving larger wavenumber shifts to lower values. Consideration of data points collected after heating to 573 K permits estimate values of the bridging CO singleton frequencies, which are 1912 and 1822 cm^{-1} for (μ_2) CO and (μ_3) CO, respectively. Reassuringly, these frequency shifts and singleton frequencies are comparable to those observed for DRIFTS measurements performed in the Bruker Vertex spectrometer (TIR and DRIFTS).

Regardless of spectrometer or sample cell used, Figs. 3 and 5 show comparable trends in terms of temperature induced peak shifts. This indicates that within the temperature range examined (300–573 K) the sample temperature measurement is consistent across the platforms examined. (This may not be the case for studies conducted at higher temperatures [34].) Moreover, the observed shifts in peak position broadly correspond to mass spectrometric CO temperature programmed desorption profiles observed for CO on Pd/Al_2O_3, with maximum rates of desorption exhibited in the 400–600 K region [36].

Table 2 The shift in wavenumber over low and high temperature ranges observed for the Nicolet Nexus spectrometer/SpectraTech smart diffuse reflectance accessory

IR technique	Temperature (K)	Wavenumber shift ($cm^{-1}K^{-1}$)	
		μ_2	μ_3
DRIFTS	< 423	0.1	0.1
	> 423	0.4	0.5

In comparison with the Bruker DRIFTS measurement (Fig. 2b), Fig. 4 shows the linearly bound (on-top) CO to be observable at higher desorption temperatures. Furthermore, the bridging modes between 1900 and 1980 cm^{-1} are still present at 573 K indicating the sensitivity of the Nicolet Nexus DRIFTS arrangement. Figure 6 presents the normalised absorbance values for the linearly bound CO for all three measurement set-ups considered and demonstrates the superior sensitivity of the Nicolet Nexus DRIFTS set-up. The enhanced sensitivity of these measurements is attributed to the internal reflection element of the SpectraTech Smart diffuse reflectance cell with environmental chamber which gives this arrangement a short optical pathlength (Fig. 1). Reference to Eq. 1 shows the benefit of a shorter optical pathway. Thus, a short optical path length is desirable for DRIFTS measurements, and the Nicolet Nexus spectrometer with the SpectraTech Smart diffuse reflectance cell and environmental chamber meets this requirement. The Bruker

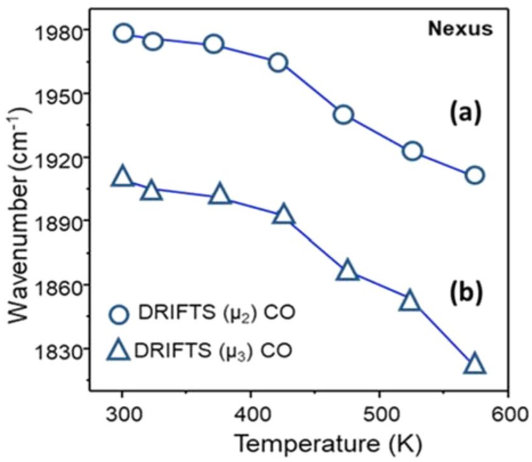

Fig. 5 Variation in the wavenumber values for (**a**) (μ_2) and (**b**) (μ_3) bound CO upon increasing temperature using the Nicolet Nexus spectrometer

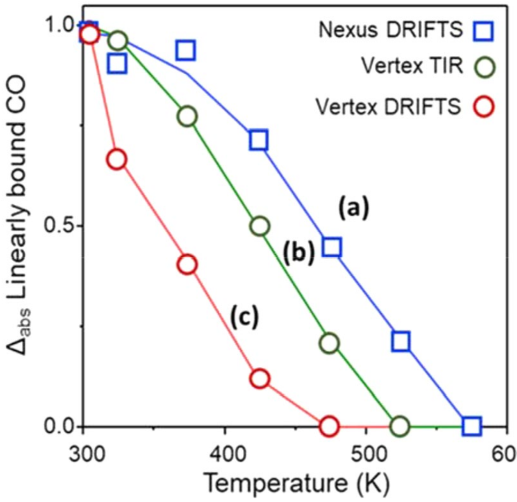

Fig. 6 Variation in the absorbance values for linearly bound CO upon increasing temperature: **a** Nexus DRIFTS, **b** Vertex TIR, **c** Vertex DRIFTS

Vertex spectrometer equipped with a Harrick Praying Mantis diffuse reflectance cell and high temperature reaction chamber demonstrated lower sensitivity. For reasons discussed above, the optical design of the cell is in part responsible for this. It is the optical efficiency of the particular sampling accessory rather than spectrometer performance that is thought to be primarily responsible for the observed spectral sensitivity. Nonetheless, despite demonstrating a lower sensitivity than the Nicolet Nexus set-up, the Bruker Vertex/Harrick diffuse reflectance accessory set-up is still highly satisfactory for use in FT-IR measurements of supported metal catalysts. Indeed, the Harrick accessory offers the advantage of being readily transferable between different spectrometer configurations, whereas the SpectraTech DRIFTS accessory considered here is explicitly linked to the Nexus spectrometer. It is often useful in catalysis laboratories to be able to interchange analytical equipment.

In the context of the emerging *operando* movement within the heterogeneous catalysis research community, the DRIFTS sampling option enjoys wide popularity [37]. However, this study reiterates the point made by Holmes et al., that one should be aware that different IR sampling arrangements can affect spectral outcomes [20]. Indeed, this perspective can be exasperated when comparing relatively intense and weak transitions within the same spectrum. For example, as exemplified by McInroy et al. in their use of vibrational spectroscopy to investigate the interaction of methanol on η-alumina [38], an adsorbate combination band at about 2600 cm^{-1} was relatively strong in DRIFTS spectra but considerably weaker in the corresponding TIR measurement. This occurred due to the inherently weak combination mode being effectively optically thin in transmission mode but optically thick in a diffuse reflectance mode [38].

Finally, a further outcome of this study is a consideration of being able to observe how linear bound CO molecules can provide information on metal edge and corner sites. These sites are implicated in the supply of hydrogen atoms for selective hydrogenation reactions [10, 15, 17]. A greater awareness of metal crystallite morphology is helpful in catalyst characterisation strategies that can then be correlated with catalytic performance to advance structure activity relationships for specified reactions.

4 Conclusions

A comparative IR study of CO desorption on a Pd/Al$_2$O$_3$ catalyst was undertaken to consider how different acquisition geometries and instrumentation may affect spectral outcomes. The main conclusions are as follows:

- For the Bruker Vertex 70 spectrometer, TIR (with a Harrick High Temperature transmission cell) and DRIFTS (with a Harrick Praying Mantis diffuse reflectance cell and high temperature reaction chamber) spectra proved to be comparable. However, bridge bonded CO was observable at higher desorption temperatures for the TIR set-up than that observed with the DRIFTS configuration. This indicates the selected TIR set-up to offer a more sensitive arrangement for CO chemisorption measurements on the Pd/Al$_2$O$_3$ sample than the designated DRIFTS set-up.
- The Nicolet Nexus spectrometer with SpectraTech Smart diffuse reflectance cell and environmental chamber demonstrated optimised sensitivity for observation of CO on Pd. This set-up was able to discern linear CO adsorption on corner and edge Pd sites. In contrast, only a single linear CO band was observable with the Bruker DRIFTS and TIR set-ups.
- Diffuse reflectance IR spectroscopy is well suited to investigate adsorption phenomena on heterogeneous catalysts. However, on occasion, it may be beneficial to additionally perform transmission measurements to understand spectral outcomes more comprehensively.

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Data Availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors have no conflict of interest.

Research Involving Human and Animal Rights There were no human or animal subjects involved in this research.

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