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Infrared study of crotonaldehyde and CO adsorption on a Pt/TiO_2 catalyst

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A Pt/TiO_2 catalyst has been subjected to reduction in hydrogen at 473, 573 and 773 K and the various degrees of metal–support interaction (SMSI) confirmed by means of CO and H_2 chemisorption, FTIR of CO and the hydrogenation of crotonaldehyde. Coadsorption of CO and crotonaldehyde were performed to identify the preferred adsorption site and mode of adsorption of the unsaturated aldehyde. Results which appear to suggest shifts to lower frequencies of bands due to adsorbed carbonyls are not due to electronic effects induced by coadsorption, but rather indicate displacement of CO from the weaker bonding sites which eliminate dipole coupling effects between different carbonyl clusters, and consequently removes intensity transfer phenomena leading to enhancement in intensity at lower frequencies.

Keywords: FTIR, Pt/TiO_2, crotonaldehyde hydrogenation, CO adsorption

1. Introduction

The hydrogenation of α,β-unsaturated aldehydes has received much attention, due to the academic challenge involved with selective hydrogenation of functional groups [1–4]. Of great importance is the determination of the modes of adsorption of the α,β-unsaturated aldehyde and the nature of its preferred adsorption sites. Theoretical [5,6] and experimental studies [7,8] have been conducted using specific single crystal faces of platinum in both monometallic and alloyed forms, however, less attention has been given to supported metal catalyst surfaces and fewer specifically deal with catalysts in an SMSI state. The use of supported catalyst to study adsorption modes involves many complications, among which is that adsorption of the C=C or C=O double bond parallel to the surface as a prerequisite to hydrogenation renders the stretching modes IR inactive. Additionally, the major part of the adsorption tends to occur on the surface of the support and this may lead to the formation of carboxylates and other adsorbed species. The IR spectrum becomes dominated by spectator species which make detection of adsorption on the active catalyst component more difficult. Infrared spectroscopy of adsorbed CO may be used to provide information regarding size and morphology of metallic particles and the extent of interaction with the support, other promoters and coadsorbates [9–13]. In the present study, experiments have been performed involving the coadsorption of CO and crotonaldehyde to derive information both relevant to the metal–support interaction and the interaction of these components with the α,β-unsaturated aldehyde.

2. Experimental

1% Pt catalyst was prepared by impregnation of Degussa P-25 Titania with an aqueous solution of hexachloroplatinic acid followed by drying in air at ca. 393 K. The sample was calcined in a flow of air for 4 h at 673 K. Prior to characterisation or reaction studies, an *in situ* reduction treatment was performed in flowing H_2 (100 $cm^3\,min^{-1}$): **A** for 1 h at 473 K, **B** for 2 h at 573 K, and **C** for 2 h at 773 K.

FTIR experiments were conducted using a quartz cell fitted with CaF_2 windows and an external furnace. Catalyst samples of 75 mg were prepared in the form of 25 mm diameter, self-supporting discs. After reduction, the cell was evacuated for 20 min with the disc at reduction temperature, before cooling to 298 K. Pulses of CO and/or crotonaldehyde were introduced at 298 K and spectra recorded using a Perkin Elmer 1720X spectrometer. Crotonaldehyde (CROALD) was purified by repeated fractional distillation under reduced pressure. Two procedures were adopted in coadsorption experiments. In the first (CO-CROALD), CO was introduced initially followed by 15 min evacuation at 298 K followed by introduction of CROALD pulses corresponding to low and high coverages of the surface (ca. 10 and 300 μmol/g-cat, respectively). The second procedure (CROALD-CO) involved adsorbing CO on a sample which had previously been exposed to quantities of CROALD again equivalent to low and high surface coverages. CO was introduced 15 min after exposure to the low coverage pulse whereas 2.5 h elapsed following exposure to the larger pulse. In both cases, spectra were recorded following brief evacuation of CO at 298 K.

The number of exposed surface platinum atoms in the catalyst was determined by H_2 and CO chemisorption at 298 K. The average Pt particle size, d (in nm), was

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calculated from the dispersion, D, using the relationship $d = 1.08/D$.

The vapour-phase hydrogenation of crotonaldehyde at atmospheric pressure and 313–373 K was studied using a dynamic flow microreactor with automatic on-line GC fitted with a Carbowax 20 M 58/90 semicapillary column. Catalysts (ca. 100 mg) were reduced *in situ* and cooled to 313 K under H_2. Catalysts were exposed to the reaction mixture in a flow (50 cm^3 min^{-1}) containing purified hydrogen and crotonaldehyde (>99.5% purity, Fluka), prepared by passing hydrogen through a thermostabilized saturator (293 K) containing the aldehyde. When the steady-state activity was obtained, the reaction temperature was raised and measurements performed at the new temperature.

3. Results

3.1. Chemisorption of H_2 and CO

Table 1 summarises results of chemisorption experiments. The lowering of chemisorption capacities of platinum obtained from both H_2 and CO uptakes indicates that the state of strong interaction between the metal and the titania is enhanced by an increase in reduction temperature. For catalyst after treatment **A**, high uptakes of both CO and hydrogen reflect a high dispersion and indicate a lack of significant SMSI state. On the other hand, catalyst after reduction **B** gave a lower chemisorption capacity, showing that the higher reduction temperature had led to a loss in dispersion. The loss in sites with ability to chemisorb hydrogen was greater than the loss for CO adsorption. Reduction at 773 K (**C**) led to a more significant loss in exposed Pt sites capable of adsorbing either adsorbate which is consistent with the catalysts having entered an advanced state of SMSI.

3.2. Hydrogenation of crotonaldehyde

The influence of the sample pretreatment temperature is reflected in the behaviour of the hydrogenation reaction (table 2). Although platinum is known to be unselective in α,β-unsaturated aldehyde hydrogenation, Pt/TiO$_2$ reduced at the lowest temperature (**A**) and apparently (table 1) not in an SMSI state, exhibited a reasonable selectivity towards C=O hydrogenation. Samples following pretreatment procedures **A** and **B** exhibited similar activities at 313 K while the sample reduced at the highest temperature (**C**) was 15 times less active as a result of the induced SMSI state. However, the catalyst was significantly more active on the basis of exposed Pt atoms (TOF) and exhibited the highest selectivity to the unsaturated alcohol. The effect of reaction temperature on the specific activities for the sample pretreated using procedures **A**, **B** and **C** was in accordance with previous studies [1,3] with TOF's of 0.021, 0.073 and 0.873 s^{-1}, respectively, at 353 K. Selectivities to other reaction products (butanol and butane) were very low.

Table 1
Hydrogen and CO uptakes obtained by chemisorption measurements.

Sample pretreatment	H_2 (μmol/g-cat)	CO (μmol/g-cat)	H/Pt	CO/Pt	d (nm) H (CO)
A (473 K)	22.1	40.7	0.86	0.79	1.3 (1.4)
B (573 K)	9.7	31.1	0.38	0.60	2.8 (1.8)
C (773 K)	0.9	0.8	0.04	0.02	27.0 (54.0)

Table 2
Results for the catalytic hydrogenation of crotonaldehyde at 313 K.

Sample pretreatment	Activity (μmol/g-cat)	X_{CROALC} (%)	TOF[a] (s^{-1})	Conversion (%)	E_{ac} (kJ/mol)
A (473 K)	42.1	25.3	0.008	2.8	29
B (573 K)	41.0	38.8	0.020	1.4	32
C (773 K)	2.9	50.6	0.158	0.3	43

[a] Based on hydrogen chemisorption.

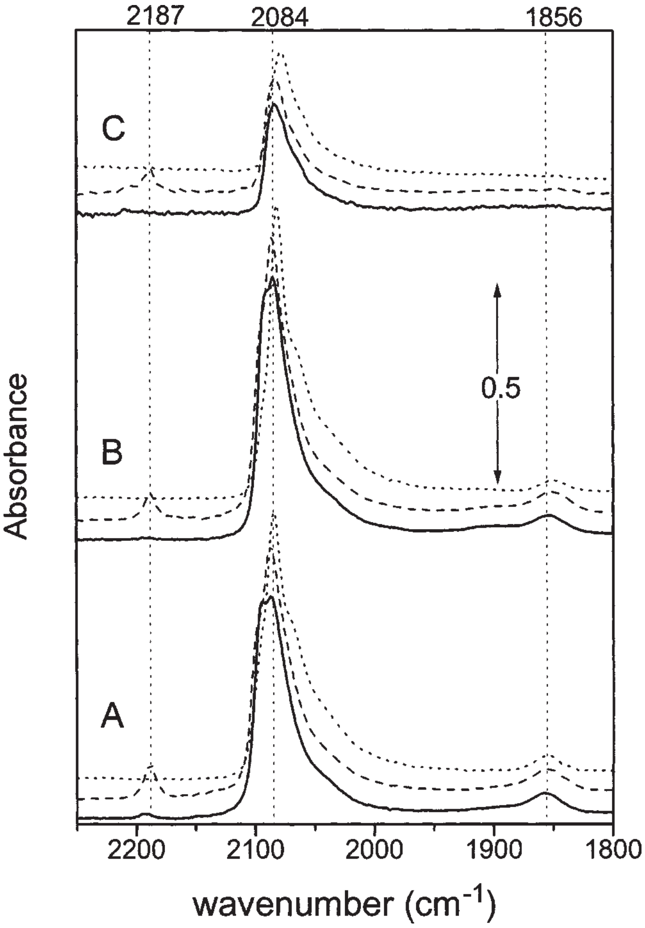


Figure 1. Infrared spectra of Pt/TiO$_2$ reduced at (A) 473, (B) 573 and (C) 773 K, exposed to 0.5 (—) and 20.0 (- - -) Torr CO and 15 min outgassing at 298 K (· · ·).

3.3. FTIR of adsorbed CO

Figure 1 shows spectra obtained for samples subjected to the reduction treatments, **A**, **B** or **C**, then subsequently exposed at 298 K to CO at 0.5 and 20 Torr followed by evacuation for 15 min. Spectra of Pt/TiO$_2$ reduced at 473 K (**A**) contain three bands at 2094, 2084 and 1856 cm^{-1} in addition to low frequency shoulders on the main band which became more pronounced on increasing the pressure of CO. An increase in intensity at 2087 cm^{-1} accompanied this increase in pressure while the higher frequency component (2094 cm^{-1}) becomes less pronounced. A band appears at 2187 cm^{-1} due to CO adsorbed at exposed Lewis acid sites in the titania surface but was absent following evacuation at 298 K. This treatment further reduced the intensity of the band at 2094 cm^{-1} component and shifted the overall maximum to lower wavenumbers. The two lower frequency shoulders were more prominent following degassing and could be deconvoluted to give bands at ca. 2070 and 2040 cm^{-1}. During these changes in CO pressures, the band at 1856 cm^{-1} superimposed on a very weak broader band ranging from 1950 to 1800 cm^{-1} due to bridging carbonyls, remained invariant although some loss in intensity accompanied evacuation.

The bands in spectra for catalyst after reduction **A** were similar to bands appearing at 2090, 2084 and 1853 cm^{-1} for the sample reduced at 573 K (**B**). Following outgassing, the 2084 cm^{-1} band remained the most prominent maximum but was shifted to 2081 cm^{-1} and, again, lower frequency shoulders were evident at ca. 2070 and 2047 cm^{-1} indicating a degree of similarity between the 473 and 573 K pretreated samples. Consistent with the reduced CO uptakes observed for 773 K reduction (table 1), IR band intensities were significantly attenuated following pretreatment **C** with a single maximum at 2082 and a shoulder at ca. 2065 cm^{-1}. There was no band at 1856 cm^{-1}. Brief outgassing at 298 K shifted the main maximum to 2078 cm^{-1}.

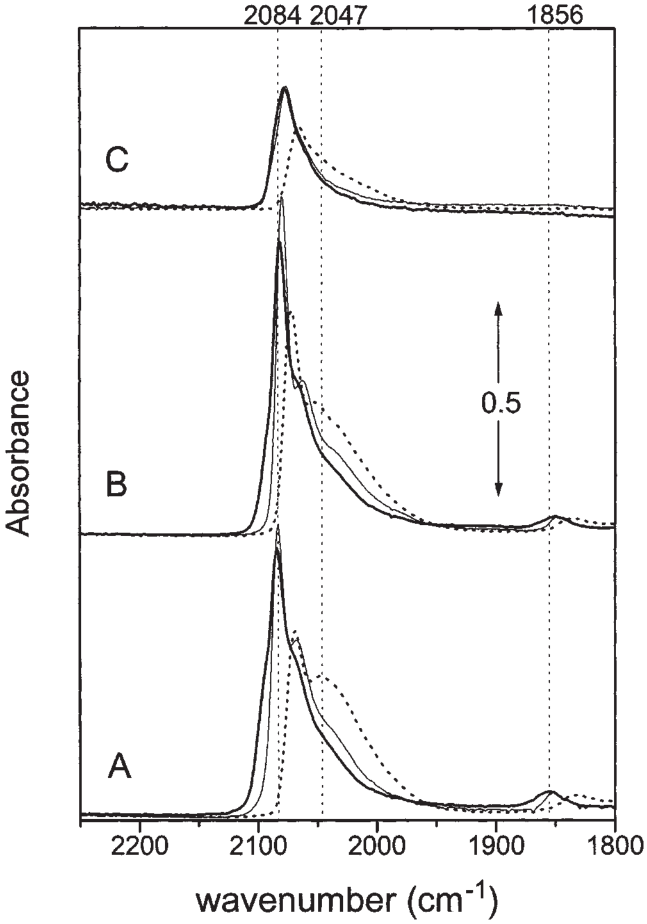


Figure 2. Infrared spectra of Pt/TiO$_2$ reduced at (A) 473, (B) 573 and (C) 773 K, exposed to 20.0 Torr CO and outgassed at 298 K for 15 min (—) followed by introduction of a low coverage CROALD pulse (—) and a high coverage CROALD pulse (- - -).

3.4. Coadsorption of CO and CROALD

3.4.1. CO-CROALD

Figure 2 displays spectra in which samples were exposed to CO and also samples which were exposed to CO and subsequently to pulses of crotonaldehyde (corresponding to low and high coverages). Irrespective of the pretreatment condition, interaction of crotonaldehyde with a CO-covered surface results in a red shift in wavenumber for the low frequency linear and bridged carbonyl bands. The sample reduced at 473 K (**A**) following the introduction of CROALD to a CO-covered surface, presents well-defined IR bands which for CO alone were detected only as shoulders. The 2084 cm^{-1} band for CO alone reflects carbonyls which were apparently unaffected by small quantities of aldehyde whereas the band at ca. 2070 cm^{-1} present only as a shoulder for CO alone, was enhanced and resolved after coadsorption. At higher CROALD coverages, the high frequency (ca. 2094 cm^{-1}) band observed for CO alone was completely removed while further enhanced intensity at ca. 2070 and 2047 cm^{-1} allowed these previously undefined shoulders to become resolved into distinct maxima. The band due to bridging carbonyls was red-shifted by ca. 5 and 25 cm^{-1}, without significant loss in intensity by low and high coverage aldehyde pulses. However, the apparent shift shown by linear carbonyls appears to result from enhanced intensities of bands already corresponding to carbonyls also present on the aldehyde-free surface. The behaviour of the sample reduced at 573 K (**B**) was very similar to effects observed for the 473 K reduced catalyst with slight variations in frequencies and bands showing overall greater intensities. For the high temperature (**C**) treated sample, no high frequency maximum was observed and the band initially at 2078 cm^{-1} was displaced to 2068 cm^{-1} in the presence of crotonaldehyde, with an accompanying loss of intensity but increase in band width. The band maximum for perturbed linear carbonyls coincides with the maxima (ca. 2070 cm^{-1}) observed for the lower temperature pretreated samples while the tail on this band extending to lower frequencies coincides with the 2047 cm^{-1} band which was better resolved for samples which had undergone reductions (**A**) or (**B**).

3.4.2. CROALD-CO

Spectra obtained by introducing CO after previously exposing the surface to amounts of crotonaldehyde corre-

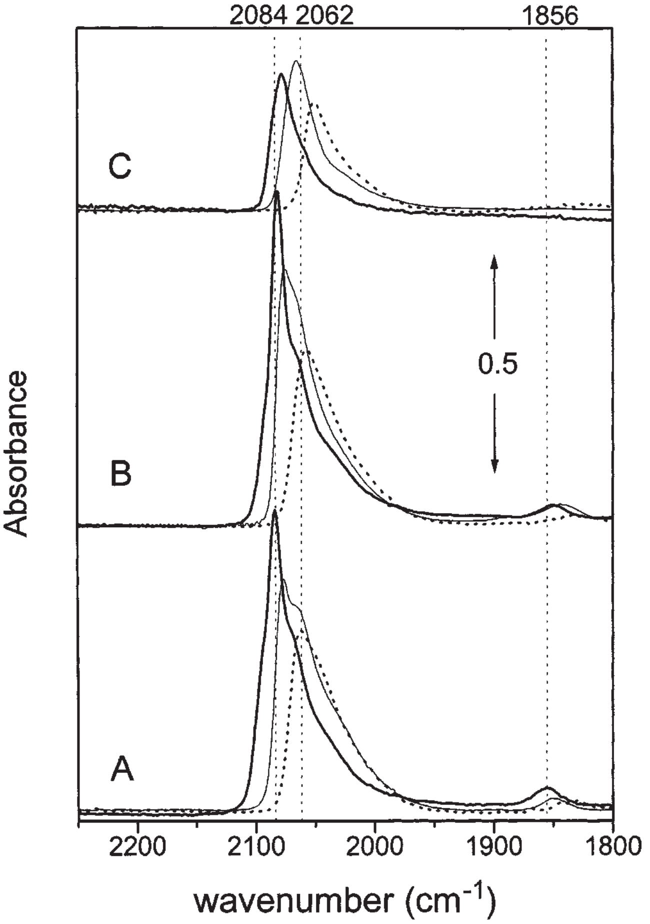


Figure 3. Infrared spectra of samples reduced at (A) 473, (B) 573 and (C) 773 K, exposed to 20 Torr CO followed by 15 min outgassing at 298 K for CROALD-free surface (—), low coverage CROALD (—) and surface pretreated with a high CROALD coverage (- - -).

sponding to low and high coverage are shown in figure 3. Spectra of CO adsorbed on a crotonaldehyde-free surface followed by evacuation for 15 min are shown for comparison. For low coverages of CROALD on the 473 K reduced surface (**A**), the spectra show a similar form to CO on the aldehyde-free surface but the bands were displaced from 2084 and 2070 (sh) cm^{-1} for the latter to 2077 and 2067 (sh) cm^{-1}. For higher aldehyde coverages, the maximum appears at 2062 cm^{-1}. The band due to bridging carbonyls was less intense and red-shifted by 10 and 20 cm^{-1} for the aldehyde-pretreated surfaces. Spectra obtained for CROALD-treated catalyst reduced at 573 K (**B**) showed similar carbonyl spectra to the 473 K reduced sample both in terms of changes in relative intensity and frequency. The 773 K reduced sample (**C**) shows a less complex spectrum, with the dominant maximum at 2078 cm^{-1} for the aldehyde-free surface progressively displaced to 2064 and 2051 cm^{-1} on chrotonaldehyde-treated surfaces with low and high coverages, respectively. Slight changes to intensity but minimal modifications to band shape accompanied these frequency shifts.

4. Discussion

Results obtained by CO and H_2 chemisorption and for the hydrogenation of crotonaldehyde clearly indicate the influence of the metal–support interactions between platinum and titania induced by reduction. From a dispersion of ca. 80% for the 473 K reduced sample, a decrease by half (H/Pt = 0.38) caused by a 100 K increase in reduction temperature cannot be attributed to loss of surface by sintering but instead reflects platinum coverage by TiO_x entities [1,14,15]. The interaction with the support is enhanced following treatment **C**, almost resulting in complete inhibition of adsorption for both hydrogen and CO.

Catalytic measurements confirm that the catalyst has been modified during the reduction procedures as platinum in the absence of support does not show selectivity in the hydrogenation of the C=O double bond [1]. The influence of the support is noticeable even for the 473 K reduction for which a selectivity of 25% towards the unsaturated alcohol is obtained. This may be interpreted in terms of the high dispersion, hence large number of metal–support interface sites present even for a catalyst which does not otherwise exhibit characteristics of a catalyst in an SMSI state. The effect of increasing the reduction temperature on catalytic behaviour gives further evidence for a catalyst in various degrees of SMSI. This is reflected in both the increase in selectivity to the unsaturated alcohol and the increase in TOF as a function of increasing reduction temperature (table 2).

Several models have been proposed to explain modification of selectivity induced by catalysts in the SMSI state [1,15]. Suboxides formed during reduction expose unsaturated cations located in close proximity to metallic platinum sites where the former can act as electron acceptor sites. The C=O bond, being the most nucleophilic part of the molecule, interacts with the Lewis acid sites, reducing the electron density of the carbonyl bond and facilitating the hydrogenation by atomic hydrogen at adjacent Pt sites. Englisch et al. [3] observed that increasing the particle size gave increased selectivity towards the unsaturated alcohol which was attributed to the greater proportion of Pt(111) surfaces presented by the larger particles, which favours adsorption via the carbonyl bond. The importance of these sites may be less significant in the current study given the high value for the initial dispersion. Other studies have focused on the possible effect of the support in influencing the electron density on the platinum [16,17]. Although this effect might be of greater significance for highly dispersed metal particles, its importance has been rejected in the selective hydrogenation of unsaturated aldehydes [2].

FTIR provided further information regarding the state of the samples after reduction. Although a loss in intensity of bands due to adsorbed CO as a function of increasing reduction temperature may be expected given the progressive decrease in CO uptakes observed (table 1), not even a qualitative relationship is observed (figure 1). The lack of correlation between adsorption capacity and integrated absorption intensities may be interpreted in terms of variations in absorption coefficients between the various carbonyl species and the influence of dilution of the exposed Pt faces by titania suboxides which disrupt the dipole coupling fields between distinct carbonyl species [18]. For linearly bound carbonyl species, absorption coefficients are greater for Pt/TiO_2 than for Pt/SiO_2 or Pt/Al_2O_3 [19]. This has been explained in terms of electron density effects on Pt induced by interactions with the support. On the other hand, the progressive shift in maximum (2087 to 2082 cm^{-1}) on increasing the reduction temperature from 473 to 773 K could be interpreted in terms of decreased dipole–dipole interaction between carbonyls as a consequence of the partial covering of the metal surface with TiO_x.

Band assignments can be made from single crystal studies considering coordination number and the number of neighbouring sites likely to result in coupling interactions [18,20,21]. The highest frequency band observed for Pt (2094 cm^{-1}) can be attributed to CO adsorbed on close packed terrace sites such as (111) patches where the carbonyls experience the most extensive dipole coupling interactions. The band at ca. 2084 cm^{-1} may be associated with carbonyls on terrace sites which are less extended or where the metal atoms are in a less dense close packing arrangement such as in the (100) face. The lower frequency bands at ca. 2065 and 2030 cm^{-1} probably reflect sites located on edges and kinks [11,12,18,20], the former band corresponding with the frequency of carbonyls located at the edges of extended (111) faces [11,21]. In summary, the IR and chemisorption values for the 473 K reduced sample indicate that the Pt is highly dispersed with a large proportion of sites of low coordination, but with a proportion of atoms located in (111)-like terraces.

Tanaka and White [22] report the surface of their 2% Pt/TiO_2 catalysts to be composed mainly of (111) faces. However, no account was taken of the importance of intensity transfer produced by dipole coupling which has the effect of exaggerating the relative abundance of the high frequency species. Therefore although deconvolution (figure 4(a)) indicates the contribution of these species to be ca. 14 and 6% of the total integrated intensity of the carbonyl band envelope for the 473 and 573 K reduced samples, respectively, these terrace sites will constitute a minority of the adsorption sites on these catalysts [23]. Although the presence of such adsorption sites has been related to the preferential hydrogenation of the carbonyl group [3], selectivity for the three reduction treatments (table 2) is inversely proportional to the integrated intensity of the 2094 cm^{-1} band (figure 4(a)) indicating that crotyl alcohol is not produced by reaction on the (111) terrace sites.

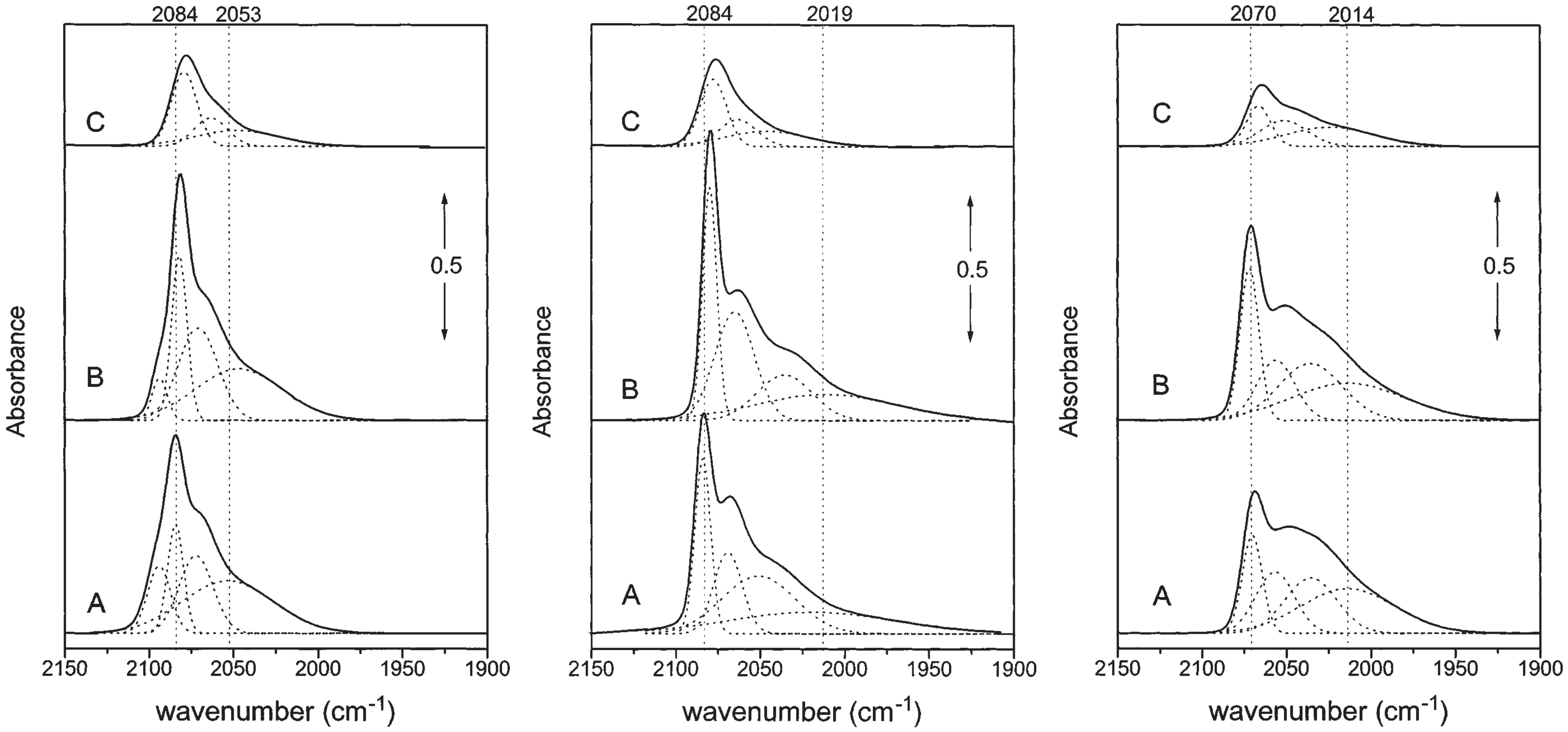
The effect of the varying degrees of SMSI state on the various carbonyl adsorption sites may be observed by comparing spectra after the three treatments. Spectra have been deconvoluted to give the least number of components which corresponds to the main band plus the number of shoulders observed visually. While a direct relationship between number of bands and types of adsorption site is unlikely due to coupling interactions between molecules on terrace and edge atoms [20], the similarity of components appearing throughout a wide range of spectra allow some degree of confidence in assigning locations where sites are depleted as coverage of TiO_x species increases. Increasing the reduction temperature from 473 to 573 and then to 773 K results in an initial decrease and then a complete loss of the 2094 cm^{-1} band, consistent with previous results for Pt/TiO_2 [22].

This behaviour can be rationalised by assuming that the suboxides of titanium have a preference for covering the densest packed platinum crystal faces in such a way that a large part of the CO molecules previously adsorbed on the (111) faces are eliminated, resulting in a progressive loss in the highest frequency carbonyl band (2094 cm^{-1}). The apparent increases in intensity of the lower frequency carbonyls following deposition of TiO_x species on the terraces can be attributed to the removal of the coupling interactions which otherwise lead to the apparent transfer of intensity from low to higher frequency bands (figure 1, (A), (B); figure 4(a), (A), (B)). The result is an increase in intensity at ca. 2084 cm^{-1} which does not result from either an increase in number of sites or increased coverage by CO at these sites. The reduction in average number of nearest neighbour sites on going from 473 to 573 K reduction is reflected in the somewhat more dramatic loss in H_2 uptakes compared with CO, consistent with the requirements for dissociative and associative chemisorption.

Following treatment **C**, a dramatic loss in adsorption capacity occurs as reflected in the low uptake values for both adsorbates and in the loss of intensity of carbonyl bands indicative of both the close packed terrace sites and the lower coordination sites. The broad nature of the bands composing the overall envelope (figure 4(a), (C)) probably indicates the rather random arrangement of TiO_x species leaving carbonyl clusters of a range of sizes. Again, the loss in area is not due to sintering of the particles present at lower reduction temperatures which would enhance the proportion of higher frequency carbonyls while in fact the opposite effect is observed. The band at 1856 cm^{-1} is associated with CO adsorbed in a two-fold-bridging mode on the close packed terrace sites [22,24]. The loss of this feature following treatment **C**, in addition to reflecting changes in the local site geometry of the remaining exposed adsorption sites, supports the concept that TiO_x coverage rather than sintering is responsible for loss of metal area and these terrace sites are the preferred location for suboxide coverage.

5. Coadsorption

In addition to displaying low chemisorption capacities, Pt/TiO_2 catalysts after high temperature reduction exhibit particularly low heats of adsorption for CO [25] making the molecule particularly sensitive to displacement by coadsorbates. On comparing deconvoluted spectra for CO alone and following the low coverage pulse of crotonaldehyde (figure 4 (a) and (b)), the three main effects for the



(a) (b) (c)

Figure 4. Deconvolution of spectra displayed in figure 2 for samples reduced at (A) 473, (B) 573 and (C) 773 K, following: (a) exposure to 20.0 Torr CO followed by desorption at 298 K for 15 min; (b) introduction of a low coverage CROALD pulse; and (c) introduction of a high coverage CROALD pulse.

473 and 573 K treated samples are the loss of the 2094 cm^{-1} band, the gain in intensity at 2084 cm^{-1} and the resolution of the 2070 cm^{-1} component. The influence of crotonaldehyde on CO on the high temperature reduced sample is less clear. Similarly, comparing the deconvoluted carbonyl spectra following low and high coverage pulses of crotonaldehyde (figure 4 (b) and (c)) shows the loss of the highest frequency (2084 cm^{-1}) component, enhanced intensity and resolution at 2070 cm^{-1}, and an increase in overall integrated intensity at ca. 2050 cm^{-1}. Again, these effects are shown for the 473 and 573 K reduced surfaces although the high coverage pulse does appear to result in significant shift to low frequency for the high temperature reduced sample (figure 4(c), (C)).

It is unlikely [22] that the enhanced intensities at lower frequencies reflect an increased coverage of the corresponding adsorption sites following displacement of CO from the terraces (2094 cm^{-1}) by crotonaldehyde. These carbonyls exhibiting a lower vibrational frequency (weaker C–O bond) represent the strongest held carbonyls (strongest Pt–C bond) which would exhibit high coverage under such conditions. Similarly, it is unlikely that the generation of further adsorption sites of such type are generated, for example, by a roughening of the surface induced by crotonaldehyde adsorption at room temperature although surface roughening induced by molecular adsorbates has been reported [26].

At first sight the spectra take on the form of a high frequency maximum with lower frequency shoulders which in the presence of increasing quantities of crotonaldehyde show a systematic displacement to lower frequencies of each component carbonyl (figure 2). There is a temptation to interpret this in terms of electronic modifications induced by coadsorption of the unsaturated aldehyde. Coadsorption has been studied [27–29] involving benzene, acetylene, ethylene and cyclohexane each of which have the potential to transfer electrons to the metal and each of which results in a shift to lower frequencies of the coadsorbed carbonyl species. The results have been interpreted [28] mainly in terms of the increased electron density on the metal providing additional back donation into antibonding 2π orbitals strengthening the metal–carbon bond but weakening the C–O bond.

The above interpretation is rejected here. Adsorption of crotonaldehyde in the presence of CO (figure 2) does not result in a random shift in frequency of carbonyl bands, but rather gives changes in intensity at fixed band positions. For example, the central band at 2084 cm^{-1} in the absence of the aldehyde (figure 4(a)) is still present at 2084 cm^{-1} in its presence (figure 4(b)), only the intensity has increased and the band at 2094 cm^{-1} has been eliminated. Addition of aldehyde to a CO-covered surface maybe expected to gradually deplete the CO overlayer leaving progressively smaller sized carbonyl clusters. When the order of adsorption is reversed (figure 3), one could envisage CO molecules initially to occupy gaps in the crotonaldehyde overlayer. If the greatest influence of coadsorption on the nature of carbonyl bonding is electronic (i.e., through metal interaction) then the resultant spectra should be indifferent to the distribution of surface carbonyl species. Through space interactions will be much more sensitive to the arrangement of carbonyls on the surface. Comparing figures 2 and 3, where the order of adsorbate addition is inverted, the spectra obtained in the low frequency (2075–1950 cm^{-1}) range are different in both shape and position. These effects can be explained completely using dipole coupling theory without the need to invoke electronic changes within the metal surface.

The effect is best illustrated by reference to CO adsorption on the Cu(755) face which consists of six atom wide (111) terraces separated by monoatomic steps [18,23]. At high coverage, the spectra show a single, high frequency band corresponding to CO adsorbed on the step [30] as a result of dipole coupling interactions which result in an intensity gain by the higher frequency mode at the expense of the lower frequency mode. In the case of platinum, this should create the impression that the proportion of terrace sites indicated by the high frequency band is always exaggerated [10,18,23]. The gain in intensity of the high frequency mode reflecting constructive interference should quantitatively match the intensity lost by the lower frequency mode which involves partial destructive interference.

Although spectra clearly illustrate this effect qualitatively, quantitative analysis is somewhat complicated by its dependence on the method and consistency of deconvolution, the complete elimination by displacement of one type of carbonyl species (highest frequency) without loss of others (lower frequency) and the fact that intensities may be modified by changes in polarisation effects. Additionally, it must be assumed that the carbonyl species which are being displaced make a minor contribution to their own band intensity.

The sum of integrated intensities of the deconvoluted features at 2094 and 2084 cm^{-1} on the aldehyde-free 473 K treated surface is 8.03 cm^{-1} (figure 4(a), (A)) but without intensity transfer (i.e., in the absence of the 2094 cm^{-1} band following CO displacement by crotonaldehyde) is 6.78 cm^{-1} (figure 4(b), (A)). Some loss in total intensity should be expected due to the loss of the contribution of the terrace site carbonyls to their own intensity. However, the values for the 573 K treated surface are 7.78 (figure 4(a), (B)) and 8.16 cm^{-1} (figure 4(b), (B)), respectively. When peak height rather than integrated intensities are used, these are 5.5 and 5.7 for the 473 K surface, and 0.68 and 0.76 for the 573 K surface.

Although quantitatively the analysis in terms of intensity transfer may not give exact agreement, possibly because of reasons outlined above, the effect is confirmed at least qualitatively by comparing the effects of the catalysts in various stages of SMSI, which, just as observed for crotonaldehyde coadsorption, has the effect of eliminating the high frequency carbonyls due to preferential elimination of the (111)-like terrace sites. In each case comparing spectra for 473 and 573 K treated surfaces (i.e., comparing **A** and **B**) there is a marked increase in intensity of the main, resolved IR band either at 2084 or 2070 cm^{-1} either in the absence of crotonaldehyde (figure 4(a)), at low relative coverage (figure 4(b)), or at high crotonaldehyde coverages (figure 4(c)). Clearly the enhanced intensity for the 573 K pretreated sample compared to the 473 K pretreated sample, in the absence of coadsorbate cannot be attributed to an increase in the number of adsorbed molecules as the CO chemisorption values indicate a 25% loss in uptake.

6. Conclusions

During reduction, TiO$_x$ species migrate to the platinum surface as indicated by decreases in H$_2$ and CO chemisorption, changes in activity and selectivity in crotonaldehyde hydrogenation, and, for high reduction temperatures, loss in intensity of IR bands due to adsorbed CO. The latter indicates that the initial losses in Pt surface occur at the closed packed (111)-type terrace sites. In the same way that TiO$_x$ preferentially blocks the sites giving the weakest adsorbed forms of CO (and thus the highest frequency carbonyl) the adsorption of crotonaldehyde initially displaces CO from these sites. Evidence from IR of adsorbed CO concerning the relative abundance of the various adsorption sites is distorted by intensity transfers resulting from dipolar coupling interactions.

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