IR study of CO adsorption on Pt, Re and Pt–Re/Al$_2$O$_3$ catalysts before and after coking

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Abstract

Infrared (IR) spectra are reported of CO adsorbed on alumina-supported Pt, Re and Pt–Re catalysts before and after coking by exposure to heptane at 683 K. For Pt, dominant sites for linear CO were in short terraces akin to those in high index planes. For Re, initial adsorption on three-dimensional crystallites giving Re$^{\circ}$–CO was followed by slow carbonylation leading to Re$_2$(CO)$_{10}$, Re(CO)$_3$ and possibly Re(CO)$_5$ on the alumina support. The formation of Re(CO)$_3$ was promoted by higher precalcination temperature before catalyst reduction. For Pt–Re, all the effects characteristic of the separate catalysts were observed. The Pt dispersions were similar for Pt alone and Pt–Re. However, the availability of Re sites was considerable enhanced in the mixed system. Short terraces on Pt or Pt–Re particles did not contain Re atoms, which were located at kink or edge sites on the particles or were spread in a phase consisting mainly of Re over the alumina surface. Coking of Pt was greater than that of Re, although the latter was enhanced for Pt–Re. Small patches of uncoked Pt were enlarged after addition of CO at 293 K showing CO-induced mobility of the carbonaceous layer. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The addition of rhenium to Pt/Al$_2$O$_3$ catalysts hinders coking during hydrocarbon reforming reactions [1,2], in particular controlling coke deposition at sites beneficial to catalysis [3,4]. Coke is deposited on both the metal and support catalyst components [5], coking of the metal having been related to catalytic function at kinked edge sites and terrace sites in exposed metal surfaces [4]. Attempts to understand coking of Pt–Re catalysts is not helped by contro-versy concerning whether the metal components are alloyed [6–10] or not [11–13], and whether the rhenium component is completely reduced [12,14–16]. A mechanism for alloy formation has been proposed [17]. Catalyst preparation influences the extent of Pt–Re interaction [18], which in turn influences coking in the sense that more interaction leads to less coking [19]. The reducibility of rhenium alone on alumina is also affected by preparative method [15,20–23]. Although platinum has been reported to promote rhenium reduction in mixed catalysts [10,24,25] this has been disputed [15] with the argument that the key factor in rhenium reduction is the

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hydration of the precursor metal oxide. This conclusion is consistent with data for rhenium alone [21]. Rhenium in $Pt–Re/Al_2O_3$ may not be fully reduced, ReO_2 dispersed on the alumina support having been observed [12,16]. Rhenium can exist on alumina either as a two-dimensional dispersed phase which can only be reduced by hydrogen to Re° at $> 500°C$, or as a three-dimensional phase which is more readily reduced [26]. Two sizes of dispersed Pt particle in $Pt–Re/Al_2O_3$ have been observed [12].

The present project involved use of infrared (IR) spectra of adsorbed CO to identify surface sites in $Pt–Re/Al_2O_3$ catalysts prepared by two methods, and to explore the effects of coking of the sites by high temperature treatment with heptane. Previous studies of CO on similar catalysts [6–8,27] have not been concerned with coking, apart from work on the build-up of carboxylate species on the alumina support [28]. The beneficial effects of sulphur on $Pt–Re/Al_2O_3$ catalysts under industrial reforming conditions are not explored here.

2. Experimental

Catalysts containing 0.3 wt.% Re, 1.0 wt.% Re, 0.3 wt.% Pt, and 0.3 wt.% Re + 0.3 wt.% Pt supported on γ-Al_2O_3 (Degussa, surface area 110 m^2 g^{-1}) were prepared by wet impregnation of alumina with aqueous solutions of $Pt(NH_3)_4(OH)_2$ and Re_2O_7 (both Johnson Matthey), followed by evaporation of the solvent and drying at 383 K. Two Pt–Re catalysts were prepared, one by co-impregnation (Pt–Re(C)), and one involving step-impregnation (Pt–Re(S)) where addition of Pt was followed by calcination in air at 673 K before subsequent impregnation with Re.

Self-supporting discs of catalyst precursor were placed in an infrared cell with fluorite windows and calcined for 1 h in a flow (100 cm^3 min^{-1}) of dry CO_2-free air at 763 or 843 K, before reduction for 1 h in a hydrogen flow (100 cm^3 min^{-1}) at 763, 893, 943 or 983 K.

Unless otherwise stated the results presented were for calcination at 763 K and reduction at 893 K. Reduction was followed by evacuation at the same temperature and cooling to ca. 293 K before admission of CO and recording of the IR spectrum using a Perkin-Elmer 1710 FTIR spectrometer at 4 cm^{-1} resolution. Coking involved exposure of reduced catalyst at 683 K to heptane vapour (267 N m^{-2}) for 30 s, and was followed by rapid cooling to ca. 293 K, evacuation and admission of CO. For comparative purposes a fixed CO pressure of 4.00 kN m^{-2} was admitted to both uncoked and coked catalysts.

3. Results

3.1. Pt/Al_2O_3

Deconvolution showed that the band envelope for CO on Pt/Al_2O_3 was best resolved into three separate maxima as in Fig. 1 for catalyst calcined and reduced at 843 and 943 K,
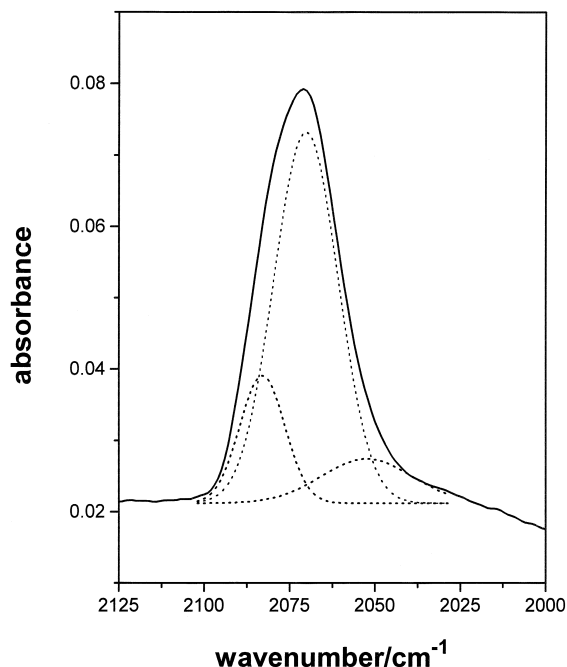

Fig. 1. Band envelope deconvolution for CO on Pt/Al_2O_3 after 843 K calcination and 943 K reduction.

Table 1
Band positions/cm^{-1} and maximum absorbances for CO after 12 h on Pt/Al$_2$O$_3$ after 843–943 K or 763–893 K pretreatments

843–943 K (uncoked)		763–893 K (uncoked)		763–893 K (coked)	
Band	Absorbance	Band	Absorbance	Band	Absorbance
2052	0.006	2046	0.021	2028	0.008
2070	0.052	2071	0.077	2062	0.037
2083	0.018	2083	0.027	2073	0.005

respectively. Band positions and intensities at the absorbance maxima are given in Table 1. The band positions were similar for catalyst calcined at 763 K and reduced at 893 K, although all three bands were more intense for catalyst pretreated at lower temperatures, Fig. 2, Table 1. The increase in intensities for the bands at 2070 and 2083 cm^{-1} were the same ($\times 1.5$), but the band at ca. 2050 cm^{-1} was increased more ($\times 3.5$) leading to an enhancement in the half-width of the overall band envelope. All three bands are due to linear CO on Pt sites. Band positions for CO on Pt/Al$_2$O$_3$ [29–31] or Pt/SiO$_2$ [32,33] are sensitive to the quality of the Pt dispersion and hence to loading and pretreatment conditions. In general bands at high wavenumbers (here 2083 cm^{-1}) are attributed to poorly dispersed Pt associated with

Pt crystal faces [31] or large crystallites [29]. De La Cruz and Sheppard [32] have summarised the correspondence between the high frequency maxima and bands due to CO on (111) and (100) single crystal faces. The dominant band here at 2070 cm^{-1} is not associated with extended low-index crystal faces [31], but is reminiscent of maxima for CO on high index planes [32]. Bands at lower wavenumbers are ascribed to sites on highly dispersed Pt [29,30]. The lower temperature calcination and reduction pretreatment adopted here therefore favoured a better Pt dispersion giving increases in the intensities of all three bands, but particularly enhancing the band due to the most highly dispersed catalyst component. Spectra similar to those here with a dominant band at 2073 cm^{-1} have previously been reported for well dispersed (H/Pt = 0.99) Pt on alumina [30].

Coking inhibited 92% of the CO adsorption after short CO contact times, Fig. 2, and the band due to Pt–CO was shifted to 2053 cm^{-1}. However, the band maximum grew in 12 h with a five times increase in intensity and also shifted to 2062 cm^{-1}. Thus poisoning of the dominant Pt–CO species after 12 h was only ca. 52% although a higher percentage level of poisoning was observed for Pt–CO giving the IR band at
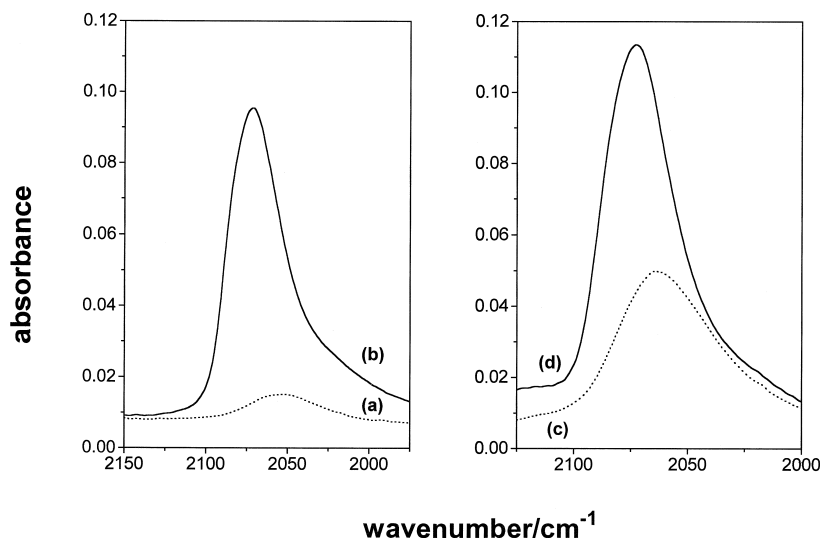

Fig. 2. Spectra after (a), (b) 2 min, (c), (d) 12 h of CO on Pt/Al$_2$O$_3$ after 763 K calcination and 893 K reduction: (b), (d) uncoked, (a), (c) coked catalyst.

2083 cm^{-1}, which together with the other two bands was shifted to lower wavenumbers, Table 1. The results conform to a model [4] in which hydrocarbon cracking occurs at kinked steps which are therefore partially poisoned, but coke growth occurs from edges across exposed crystal terraces or planes which are therefore also poisoned. The band shifts induced by coking are probably ascribable to decreases in dipolar coupling effects [7,34] because of dilution of the surface concentration of adsorption sites by coke deposition. Carbon deposits on Pt poison adsorption sites, but are apparently influenced by CO in a way which releases Pt sites for CO adsorption. Slight changes in spectra with time for uncoked catalyst, Fig. 2, were relatively insignificant compared with the results after coking.

3.2. Re / Al$_2$O$_3$

The 1% Re/Al$_2$O$_3$ catalyst was studied after calcination at 763 K and reduction at 763, 893 or 983 K, or calcination at 843 K followed by reduction at 943 K. 0.3% Re/Al$_2$O$_3$ was studied after a 763 K calcination and 893 K reduction. Addition of CO to both uncoked and coked catalysts led to spectra which varied with CO pressure, time and subsequent evacuation. Only selected results for 1% Re/Al$_2$O$_3$ are presented to illustrate the general effects.

Catalyst prereduced at 763 K gave weak spectra of adsorbed CO suggesting that reduction was far from complete. Reduction at 893 or 983 K gave much stronger bands, particularly for 893 K, suggesting that treatment at 983 K had led to sintering and loss of Re dispersion. Otherwise the two higher reduction temperatures after calcination at 763 K gave similar spectra as a function of CO pressure. Initially at low pressures a dominant band appeared in spectra at 2045 cm^{-1}, Fig. 3(a), and may be ascribed to CO linearly adsorbed on Re$^{\circ}$ atoms [35] present in three dimensional crystallites Re$_x$ of well reduced rhenium [26]. With increasing CO pressure weak shoulders increased in inten-
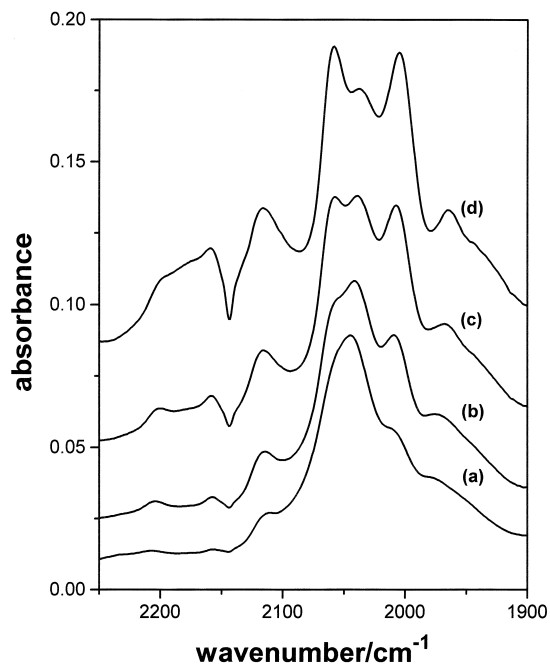

Fig. 3. Spectra of 1% Re/Al$_2$O$_3$ (calcined/reduced: 763/893 K) after exposure to CO at pressures of (a) 0.53, (b) 1.06, (c) 3.99, and (d) 10.1 kN m^{-2}.

sity until they constituted the dominant bands at 2116, 2057, 2002 and 1961 cm^{-1}, Fig. 3(d). The band due to linearly adsorbed CO remained apparent but was shifted slightly to 2035 cm^{-1}. A shoulder was also present at ca. 1933 cm^{-1}. Attempts at deconvolution of the band envelope with six component bands were much less successful than if an additional band was included at ca. 2016 cm^{-1}, although no corresponding maximum in the spectra was distinguishable. The deconvoluted band positions were 2109, 2059, 2039, 2016, 1999, 1963 and 1933 cm^{-1}. Five of these bands agree well with bands at 2127, 2073, 2015, 2009 and 1967 cm^{-1} reported by McKenna et al. [36] for Re$_2$(CO)$_{10}$ adsorbed on alumina. In accordance with more recent studies of Re$_2$(CO)$_{10}$ on alumina [37], and with the conclusions of Solymosi and Bánsági [35] for CO on Re/Al$_2$O$_3$ the present five bands are therefore ascribed to the formation of Re$_2$(CO)$_{10}$, probably ligated to Al^{3+} sites in the surface of the alumina support [37].

The weak shoulder at 1933 cm^{-1} may be associated with a further carbonyl of rhenium, possibly $Re(CO)_3$ [35–37], the other main band at 2029 cm^{-1} [36,37] due to this species being obscured by the strong bands due to $Re_2(CO)_{10}$ and linearly adsorbed CO on Re_x°. A band at 2200 cm^{-1} is due to CO weakly ligated to Al^{3+} sites in the alumina surface. A further band at 2160 cm^{-1}, which grew in intensity in parallel with the bands due to $Re_2(CO)_{10}$, could be due to CO in another rhenium carbonyl complex, possibly $Re(CO)_5$ [36,37]. The bands at 2116 and 2160 cm^{-1} were partially obscured by underlying maxima in the spectrum of CO gas.

Spectra of Re/Al_2O_3 in contact with CO at 293 K also changed with time. Fig. 4 shows a typical change from a spectrum after short contact times of CO linearly bonded to Re° sites to a spectrum after long times dominated by bands due to $Re_2(CO)_{10}$. The shoulder at 1933 cm^{-1} due to $Re(CO)_3$ was absent at first but grew into a distinct maximum, Fig. 4(b). For longer times

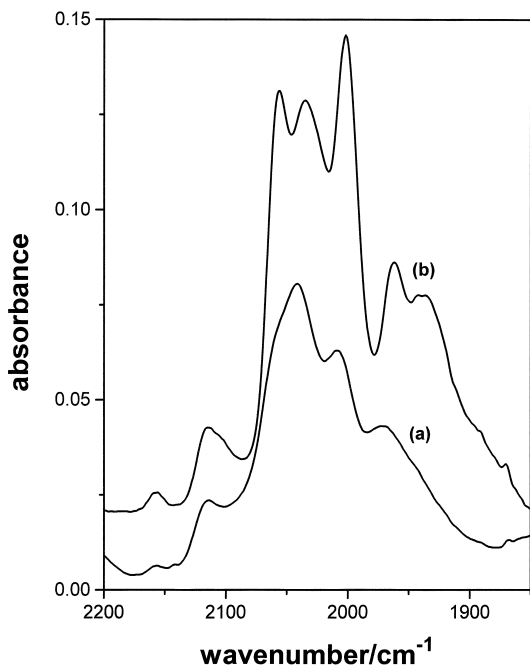Fig. 5. Spectra of 1% $ReAl_2O_3$ (calcined/reduced: 843/943 K) after exposure to CO (3.99 kN m^{-2}) for (a) 2 min, (b) 1 h, (c) 12 h.
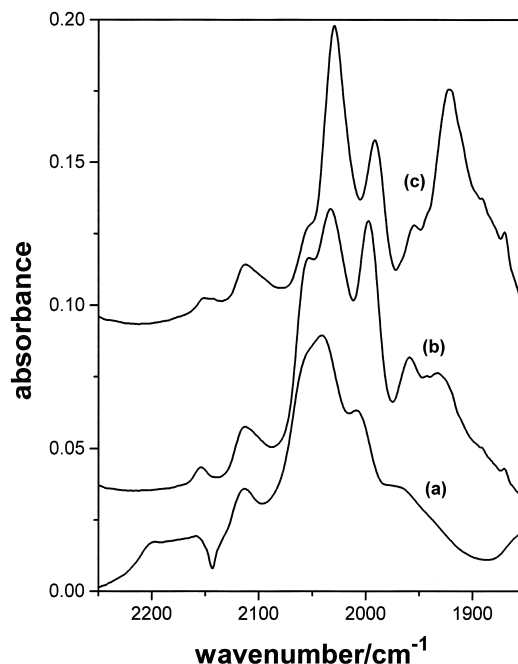

Fig. 4. Spectra of 1% Re/Al_2O_3 (calcined/reduced: 763/893 K) after exposure to CO (3.99 kN m^{-2}) for (a) 2 min, (b) 12 h.

(not shown) the band at 1933 cm^{-1} continued to grow but the maxima due to $Re_2(CO)_{10}$ started to decrease in intensity. The reaction sequence Re–$CO \rightarrow Re_2(CO)_{10} \rightarrow Re(CO)_3$ for Re/Al_2O_3 which had been calcined/reduced at 763/893 K was apparently accelerated for catalyst given the 843/943 K pretreatment. For both catalysts the generation of $Re_2(CO)_{10}$ occurred at about the same rate. However, comparison of Fig. 5(c) and Fig. 4(b) shows that the higher temperature calcination/reduction procedure greatly increased the rate of appearance of $Re(CO)_3$, which gave prominent infrared bands at 2029 and 1923 cm^{-1} [36,37]. This rate enhancement did not occur for Re/Al_2O_3 pretreated at 763/983 K suggesting that it was the increase in calcination temperature rather than reduction temperature which was responsible for enhanced $Re(CO)_3$ formation. The conversion of $Re_2(CO)_{10}$ adsorbed on alumina to $Re(CO)_3$ is also promoted by evacuation [35], high temperature [35,37] or photolysis [36].

Fig. 6 shows results for evacuation of Re/Al_2O_3 which had been exposed to a high pressure of CO. The spectrum after 1 h was characteristic of $Re(CO)_3$ with some residual $Re_2(CO)_{10}$.

Previously [35] bands at 1850–1870 cm^{-1} for Re/Al_2O_3 exposed to CO have been ascribed to bridged CO on Re. Bands appeared in the present spectra at ca. 1830 and 1860 cm^{-1}, their intensities varying with treatment conditions. For example, the bands weakened as the spectrum of CO on Re changed from Re_x°–CO to $Re_2(CO)_{10}$, and disappeared when bands characteristic of $Re(CO)_3$ appeared. However, identical bands at 1827 and 1853 cm^{-1} have been recorded for CO on alumina alone [38], and were observed here for alumina which had been subjected to the same calcination/reduction procedure as for the Re catalysts. In the present work separate bands possibly due to bridged CO on Re could not be detected. Changes of band intensity at 1830–1860 cm^{-1} may have been due to competition for sites on alumina from carbonyl complexes of rhenium.
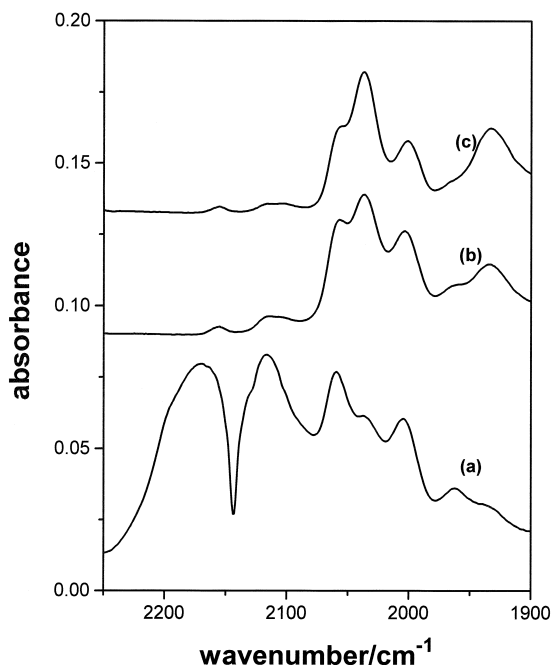

Fig. 7. Spectra of 1% Re/Al_2O_3 (calcined/reduced: 763/893 K) after coking and exposure to CO (3.99 kN m^{-2}) for (a) 2 min, (b) 12 h.

Fig. 6. Spectra of 1% Re/Al_2O_3 (calcined/reduced: 763/983 K) (a) exposed to CO (21 kN m^{-2}), and evacuated at 293 K for (b) 15 min, (c) 1 h.
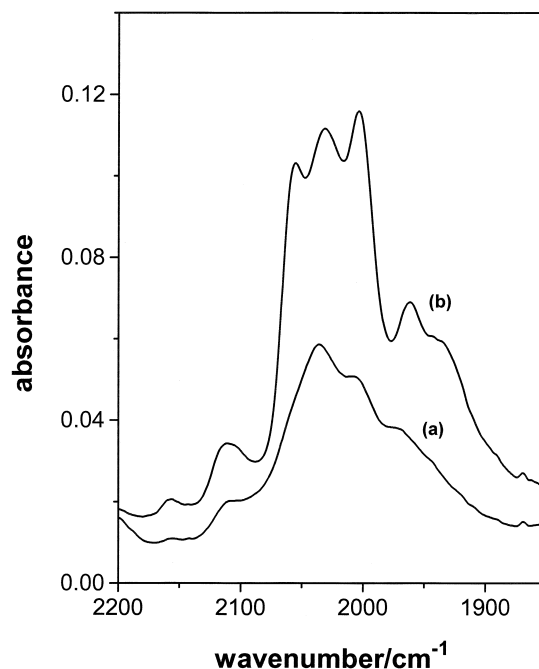
Additional strong bands resulting from CO adsorption on alumina also appeared at 1652, 1490, 1446 and 1232 cm^{-1} and are due to surface hydrogen carbonate which apparently played no part in the reactions of rhenium.

Fig. 7 shows results for coked Re/Al_2O_3 which are comparable with the corresponding spectra, Fig. 4, for uncoked catalyst. The band maximum after short contact times was at 2037 cm^{-1} and was 58% of the intensity for uncoked catalyst, suggesting that ca. 42% of Re° sites for the linear adsorption of CO had been poisoned by coking. Deconvolution showed that the band due to Re_x°–CO was at 2034 cm^{-1}, which represents a shift of -5 cm^{-1} caused by coking probably due to less significant dipolar coupling effects because of the dilution of Re sites by coke [7,34]. Both the extent of site poisoning and the accompanying band shifts due to dilution were less for rhenium than for platinum. Reaction to $Re_2(CO)_{10}$ and $Re(CO)_3$ also occurred on the coked rhenium surface,

Fig. 7(b). Typically the poisoning of complex formation was appreciably less than the poisoning of linear adsorption of CO. For example, the band intensities in Fig. 7(b) were ca. 70–75% of the intensities in Fig. 4(b) despite the much bigger difference between the band intensities in spectra 4(a) and 7(a). One inference might be that the formation of $Re_x^\bigcirc$–CO and $Re_2(CO)_{10}$ involves different rhenium sites and it is the sites giving $Re_x^\bigcirc$–CO which are the most poisoned. Yao and Shelef [26] have identified two forms of rhenium in Re/Al_2O_3 catalysts. Linearly adsorbed CO would be most likely to form on three dimensional crystallites of rhenium which would be heavily coked, whereas, two dimensional arrays of rhenium spread over the alumina surface might be less readily coked but be responsive to reaction with CO giving rhenium multicarbonyl complexes ligated to Al^{3+} ions in the alumina surface [37]. However, this is probably too simplistic a model since results for uncoked catalyst, Fig. 5, show that $Re(CO)_3$ formation is eventually accompanied by complete loss of $Re_x^\bigcirc$–CO supporting the contention [35] that disruption of Re_x crystallites by CO leads to isolated $Re^\bigcirc$ atoms and conversion of $Re_x^\bigcirc$–CO to $Re(CO)_3$.

In general the spectroscopic effects for 0.3% Re/Al_2O_3 (calcined/reduced: 763/893 K) were the same as those for the 1% catalyst. The band intensity for $Re^\bigcirc$ was decreased almost exactly in proportion to the decrease in Re loading showing that the dispersions in the two uncoked catalysts were similar. Percentage decreases in intensity accompanying coking were also similar for the 0.3% and 1% catalysts. However, the formation of $Re_2(CO)_{10}$ although still occurring appeared to be relatively less favourable for the lower loaded catalyst.

3.3. Pt–Re / Al₂O₃

Fig. 8(a) shows the initial spectrum of Pt–Re(S)/Al_2O_3 exposed to CO. The dominant band envelope maximum at 2075 cm^{-1} compares with maxima at 2073 cm^{-1} for Pt, Fig. 2,
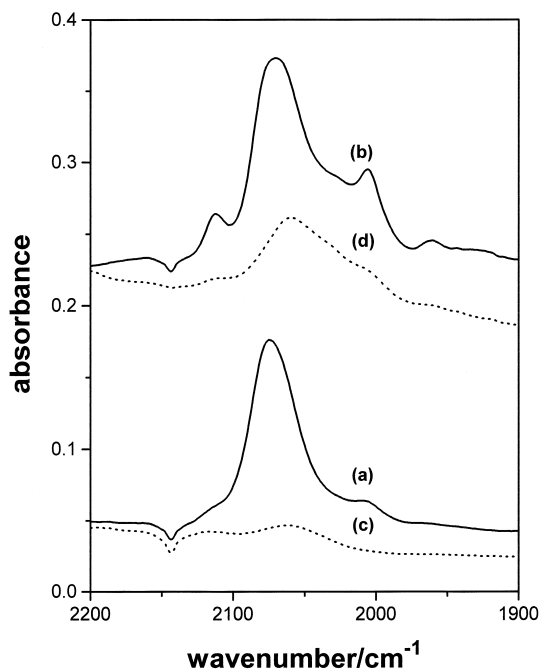

Fig. 8. Spectra of Pt–Re(S)/Al_2O_3 (calcined/reduced: 763/893 K) (a), (b) uncoked, (c), (d) coked, after exposure to CO at 3.99 kN m^{-2} for (a), (c) 2 min, (b), (d) 12 h.

and 2042 cm^{-1} for Re, Fig. 4. Comparison of band intensities for the three catalysts is informative but cannot be taken as quantitatively rigorous because of the different scattering characteristics of the catalyst discs which influences apparent band intensities. However, the maximum at 2075 cm^{-1} with absorbance 0.13 for Pt–Re(S) compared with the absorbance of 0.11 for Pt alone. With identical Pt loadings in the two catalysts the result implies that the Pt was at least as well dispersed in the mixed catalyst as for Pt alone. The $Re_x^\bigcirc$–CO band intensity for 0.3% Re was ca. 0.02 and therefore, its possible contribution to the overall band envelope for Pt–Re was relatively small. No $Re^\bigcirc$–CO band ($Re^\bigcirc$–CO represents CO ligated to a $Re^\bigcirc$ atom on an unspecified aggregate or surface layer of Re possibly on a Pt–Re particle) was detected in the spectrum for Pt–Re although it could have been present but was obscured by the dominant Pt–CO band. With increasing time bands at 2112, 2007, 1963 and 1933 cm^{-1} grew

in intensity showing that $Re_2(CO)_{10}$ was being slowly formed, Fig. 8(b). A shoulder at 2027 cm^{-1} may be indicative of Re°–CO. The maximum at 2075 cm^{-1} was shifted to 2065 cm^{-1} and grew in intensity in accordance with the expected contribution from a band at 2057 cm^{-1}, Fig. 3, for $Re_2(CO)_{10}$. For CO on Pt, dilution of the Pt surface with Re atoms would be expected to lead to a small shift to lower wavenumbers of the Pt–CO band due to reduced dipolar coupling effects [7]. This did not happen, the Pt–CO band being in the same position for the Pt and Pt–Re catalysts. Bastein et al. [7] deduced that Pt and Re were alloyed in $Pt–Re/Al_2O_3$ catalysts containing 5 wt.% total metal because the band intensities were much smaller for Pt–Re than for Pt alone although particle sizes in the samples were similar. In contrast Peri [11] observed that the interactions between CO and Pt or Re in $Pt(0.5\%)–Re(0.5\%)/Al_2O_3$ were independent of the other metal suggesting that at least a fraction of each metal was behaving in a way which was characteristic of the metal on its own. The present results for $Pt(0.3\%)–Re(0.3\%)/Al_2O_3$ were similar to those of Peri, possibly reflecting the similar low metal loadings as opposed to the much higher loadings used by Bastein et al. Bolivar et al. [6] concluded that Pt and Re were 'most probably' alloyed in Pt–Re on alumina containing 2 wt.% total metal. The infrared results alone cannot be regarded as conclusive proof for alloying or not. Pt + CO gave similar (in intensity and position) infrared band envelopes in the presence or absence of Re. Re + CO gave $Re_2(CO)_{10}$ with or without Pt present.

$Pt–Re(C)/Al_2O_3$ + CO also showed a dominant maximum at 2075 cm^{-1} due to Pt–CO after short contact times, and bands at 2112, 2007, 1963 and 1933 cm^{-1} due to $Re_2(CO)_{10}$ which grew with time, Fig. 9. The band intensities due to Pt–CO were nearly identical for Pt–Re(S) and Pt–Re(C) suggesting that the concentrations and character of exposed Pt atoms were the same in the two catalysts. However, bands due to CO ligated to Re sites were appre-
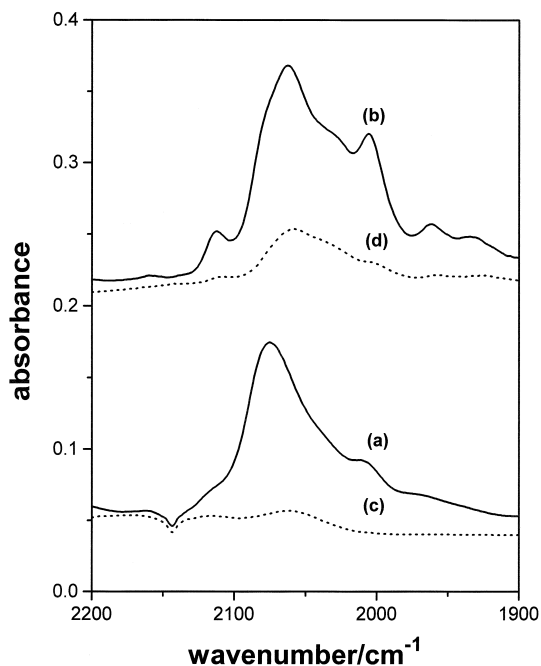

Fig. 9. Spectra of $Pt–Re(C)/Al_2O_3$ (calcined/reduced 763/893 K) (a), (b) uncoked, (c), (d) coked, after exposure to CO at 3.99 kN m^{-2} for (a), (c) 2 min, (b), (d) 12 h.

ciably more intense for Pt–Re(C) than for Pt–Re(S). The differences between the spectra for the two samples after either 2 min or 12 h could be wholly attributed to bands due to Re°–CO and $Re_2(CO)_{10}$. Band intensity comparisons show, at least for $Re_2(CO)_{10}$ formation, that about five times as much rhenium became complexed after 12 h for Pt–Re(S) than for Re alone, whereas for Pt–Re(C) the amount was about 3.3 times that for Re alone. Coimpregnation of Pt and Re apparently generated CO spectra which could be fairly well simulated by the addition of the separate results for Pt and Re in terms of band positions, but the intensities showed that the amount of Re available for complexing with CO was considerably enhanced by the presence of Pt. A smaller enhancement in available Re was apparent for the step-impregnated Pt–Re.

Spectra of Pt–Re(S) after calcination/reduction at 843/943 K were remarkably similar to the results for the 763/893 K treatment,
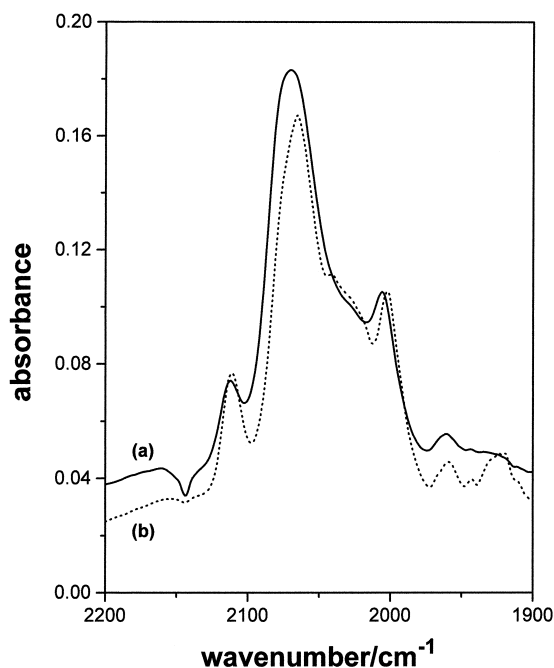
Fig. 10. Spectra of Pt–Re(S)/Al$_2$O$_3$ in contact with 3.99 kN m^{-2} CO after calcination/reduction at (a) 763/893 K, (b) 843/943 K.

Fig. 10. The extent of formation of Re$_2$(CO)$_{10}$ after 12 h was about the same. However, there was a significant decrease in intensity of the overall band envelope on the high wavenumber side which would correspond to loss of Pt–CO of the type corresponding to the dominant band for Pt alone. As for Pt/Al$_2$O$_3$, Figs. 1 and 2, the higher temperature calcination and reduction pretreatments gave weaker Pt–CO bands. Furthermore, additional bands at 1922 and 2040(sh) cm^{-1} may be ascribed to Re(CO)$_3$. High temperature pretreatment enhanced Re(CO)$_3$ formation for both Re alone, Fig. 5, and Re in Pt–Re mixtures.

For Pt–Re(C) + CO the relative intensities of the infrared bands due to Pt–CO, Re$^\circ$–CO and Re$_2$(CO)$_{10}$ were the same as for Pt–Re(S) but the bands were uniformly 33% less intense. Thus although the formation of Re$_2$(CO)$_{10}$ was more favoured for Pt–Re(C) than for Pt–Re(S) after the 763/893 K pretreatment, this effect was reversed after the 843/943 K treatment. Coimpregnation of Pt and Re followed by high

temperature treatments reduced the availability of both Pt and Re sites. The generation of Re(CO)$_3$ after prolonged contact with CO was considerably less for Pt–Re(C) than for Pt–Re(S).

Figs. 8 and 9 show the effects of coking on Pt–Re/Al$_2$O$_3$. Coking reduced the intensity of the dominant band envelope by ca. 87% for both the mixed catalysts. This represents a similar or slightly lower level of poisoning than that for Pt alone, but a bigger extent of poisoning than for Re alone. The weak maxima for coked Pt–Re were at 2061 cm^{-1} in agreement with the result for Pt alone (Table 1). The shift from 2075 to 2061 cm^{-1} induced by coking is probably primarily due to dilution of surface Pt sites and hence reduced dipolar coupling effects [7,34], although a small electronic effect due to charged carbonaceous deposit is not excluded [7]. After 2 min contact with CO bands due to Re carbonyl species were too weak to be unambiguously identified suggesting, by comparison with the results for Re alone, that Pt had promoted not only reduction of Re and therefore, generated a higher number of available Re sites, but also the poisoning of a higher proportion of the Re sites by coking. This was substantiated by the spectra after 12 h for which deconvolution showed a large reduction of intensity compared with the result for Re alone, not only for Re$^\circ$–CO but also for Re$_2$(CO)$_{10}$ formation. Unlike the results for uncoked catalysts, but in accordance with the results for coked Pt alone, the band due to Pt–CO grew with time suggesting that CO promoted Pt site regeneration after coking probably as a result of coke mobility induced by CO [39,40]. This effect was greater for Pt–Re(S) than Pt–Re(C), the poisoning of Re$^\circ$–CO and Re$_2$(CO)$_{10}$ formation also being less for Pt–Re(S) than for Pt–Re(C) after 12 h.

4. Discussion

4.1. Adsorption on Pt

The band multiplicity for CO on Pt/Al$_2$O$_3$ shows the presence of at least three types of

surface site for the linear adsorption of CO. The analogy between the band positions and bands for CO on Pt single crystal surfaces [32], combined with results for Pt/Al_2O_3 as a function of dispersion [30], suggests that the sites responsible for the dominant band were Pt atoms in short terraces similar to those in high index planes. The weaker band at 2083 cm^{-1} was due to CO on more extended terraces, whereas the band at 2050 cm^{-1} was due to CO at highly uncoordinated Pt sites, possibly either at edges or kinks between terraces [4] or in extra-small particles consisting of only a few Pt atoms [12]. The present results were consistent with spectra for highly dispersed Pt on alumina [30]. The apparent loss of dispersion for catalyst which had been calcined/reduced at 843/943 K is consistent with the effects of high temperature pretreatment of catalyst precursors in the absence of chlorine [41], which promotes Pt dispersion [42]. The catalysts used here contained no chlorine.

The complexity of the spectra of CO on $Pt–Re/Al_2O_3$ precluded reliable deconvolution of all three bands due to CO on Pt sites although the dominant band for CO on Pt could be distinguished, particularly for short contact times. The identity (± 2 cm^{-1}) of the positions of the overall band envelope maxima for Pt–CO on Pt alone and Pt–Re provides no evidence for possible electron transfer from Re to Pt atoms [6], and supports the contention [7] that there is a negligible influence of electronic effects on the metal atoms and hence the CO band positions. In fact deconvolution suggested that the Pt–CO band for Pt–Re was at ca. 7 cm^{-1} higher wavenumber than for Pt which is in the wrong direction to be compatible with the suggested [6] electron transfer. Furthermore, dilution of the terraces with Re atoms would have led to a downward shift in the band position because of decreasing dipolar coupling effects [7]. Thus arrays of Pt atoms in short terraces were apparently not diluted by the addition of Re. Bastein et al. [7] reported decreases in band intensity for CO on Pt–Re compared with Pt

alone and concluded that the Pt surface was diluted by Re. Here, in contrast, the small intensity increase for Pt–Re suggests that Re induced an increase in the population of Pt sites in short terraces, and the upward shift in band position possibly suggests that the terraces were slightly enlarged containing bigger ensembles of Pt atoms. If alloying [6–10,17] did occur in these catalysts then exposed short terraces must have retained a composition consisting entirely of Pt atoms. Peri [11] concluded from an infrared study of CO adsorption that Pt and Re behaved independently in Pt–Re catalysts. Others have studied similar catalysts for which there was no evidence for alloying of Pt and Re [12,13]. The presence of Re on terrace surfaces or at kink sites in Pt–Re has been discussed [4]. The former is not consistent with the infrared results which, however, do not preclude the latter. In support of these conclusions, heptane reforming studies of catalysts similar to those used here, but with a different pretreatment procedure, have shown that addition of 0.3% Re to 0.3% Pt on alumina enhanced hydrogenolysis selectivity [43]. Re on terrace sites may impede hydrogenolysis on Pt ensembles, whereas, Re at kink sites increases hydrogenolysis selectivity [4]. A recent infrared study of $Pt–Sn/Al_2O_3$ catalysts has similarly suggested that Sn is not randomly distributed over exposed Pt surfaces, but segregates to edge and corner sites with low coordination [30].

The behaviour of $Pt–Re/Al_2O_3$ after the 843/943 K pretreatment resembled that for Pt/Al_2O_3 lending added support for the conclusion that ensembles of Pt atoms on short terrace sites were not diluted by the presence of Re. Furthermore, for Pt and Pt–Re the high temperature treatments led to similar levels of sintering again demonstrating the insensitivity of the Pt terrace sites to Re. The effects of high temperature calcination before reduction are highly dependent on the chlorine content of Pt catalysts [41,42]. In the absence of chlorine raising the precalcination temperature leads to sintering even if the reduction temperature is kept the

same [41]. Precalcination may also lead to a weakened Pt–Re interaction in the reduced catalyst [27], therefore contributing to the lack of influence of Re on the infrared band due to CO on short-terrace Pt sites.

4.2. Adsorption on Re

The results for Re/Al_2O_3 complement the infrared study of CO on similar catalysts by Solymosi and Bánsági [35]. After short contact times the band at 2045 cm^{-1} due to $Re^{\bigcirc}$–CO confirms the presence of well reduced Re particles, in accordance with expectation [35] for high temperature oxidation followed by reduction at 893 K as generally adopted here. The only conceivable evidence for incompletely reduced Re^{n+} was a very weak band at 2160 cm^{-1} although this appeared in parallel with the bands due to $Re_2(CO)_{10}$ and was more likely to be due to the CO-induced reaction of Re as a function of time to give $Re(CO)_5$ [36,37]. Further evidence against the Re^{n+} interpretation is that the catalyst which was pretreated in hydrogen at 763 K was incompletely reduced [16] but gave negligible bands not only due to $Re^{\bigcirc}$–CO and $Re_2(CO)_{10}$ but also at 2160 cm^{-1}. The absence of bands in similar experiments was ascribed to incomplete reduction [35] implying that Re^{n+} ions do not act as sites for CO adsorption at moderate CO pressures. Nacheff et al. [44] concluded that Re^{4+} stabilised by alumina does not chemisorb CO. The infrared results do not discount the possible presence of Re^{n+} dispersed on the alumina support, although, it is likely that the proportion of Re in the unreduced state would be very small after treatment in hydrogen at 893 or 943 K [14,35].

Carbon monoxide induces the formation of $Re_2(CO)_{10}$ from Re dispersed on alumina [35]. This has been attributed to the reaction of Re_x crystallites with CO leading to smaller crystallites and eventually isolated $Re^{\bigcirc}$ atoms in Re carbonyl complexes [35]. Deconvolution of the present spectra for Re/Al_2O_3, which had been precalcined/reduced at 763/893 K, as a func-

tion of time suggested at first sight that even after 12 h reaction, when strong bands due to $Re_2(CO)_{10}$ had appeared, the intensity of the band at 2045 cm^{-1} due to $Re_x^{\bigcirc}$–CO had hardly changed in intensity. Thus the conversion of $Re^{\bigcirc}$–CO to $Re_2(CO)_{10}$ apparently only involved a small proportion of the total available $Re^{\bigcirc}$ sites. One explanation would be that the extinction coefficients of bands due to $Re_2(CO)_{10}$ are much greater than those for $Re^{\bigcirc}$–CO. However, analysis of the spectra, already difficult because of the multiplicity of bands due to $Re_2(CO)_{10}$ and $Re_x^{\bigcirc}$–CO, is further confused by the possible presence of bands due to $Re(CO)_5$. A spectrum of $Re(CO)_5$ generated from $Re_2(CO)_{10}$ adsorbed on alumina [37] shows that the broad band envelope for $Re(CO)_5$ at 2040–2012 cm^{-1} would coincide with strong bands due to $Re_2(CO)_{10}$ and more particularly the maximum due to $Re_x^{\bigcirc}$–CO. There is no clear distinguishing spectral feature for $Re(CO)_5$, against a background of bands due to $Re_2(CO)_{10}$ and $Re_x^{\bigcirc}$–CO, except possibly for the very weak band at 2160 cm^{-1}. On balance it appears that the initial adsorption of CO on $Re^{\bigcirc}$ sites was followed by the slow build up of $Re(CO)_5$ and $Re_2(CO)_{10}$, the latter being dominant. The implication that $Re(CO)_5$ contributes to the spectra leads to the conclusion that the band due to $Re_x^{\bigcirc}$–CO had been weakened during reaction although not by very much. A much bigger effect occurred for catalyst which had been pretreated at 843/943 K, Fig. 5.

Heat treatment of $Re_2(CO)_{10}$ on alumina in vacuum leads to complete decarbonylation with $Re(CO)_3$ as an intermediate species [37]. The formation of $Re(CO)_3$ also occurs for $Re_2(CO)_{10}$ generated by CO adsorption on Re/Al_2O_3, not only at 373–473 K [35] but also, depending on the pretreatment of the catalyst, at ca. 293 K. The formation of $Re(CO)_3$ was not detected at 293 K for catalyst which had been precalcined/reduced at 763/893 or 763/983 K. However, pretreatment at 843/943 K followed by addition of CO led to a reaction sequence in which the appearance of $Re_2(CO)_{10}$

was followed by $Re(CO)_3$, Fig. 5. Furthermore, spectrum 5(c) after 12 h clearly shows that the initial band in spectrum 5(a) due to $Re_x^{\bigcirc}$–CO had either been greatly weakened or had disappeared, providing strong proof for the conclusion [35] that $Re_x^{\bigcirc}$ crystallites were a precursor of adsorbed multicarbonyl complexes. The formation of $Re(CO)_3$ by evacuation of Re/Al_2O_3 exposed to CO, Fig. 6, probably resulted from decarbonylation of $Re_2(CO)_{10}$ [35–37]. However, the formation of $Re(CO)_3$ exemplified by the spectra in Fig. 5 occurred in the presence of CO and was promoted by the 843/943 K catalyst pretreatment. Both higher and lower reduction temperatures than 943 K failed to give $Re(CO)_3$ before evacuation suggesting that it was the elevation of the calcination temperature from 763 K to 843 K which was responsible for the different behaviour. Yao and Shelef [26] proposed that Re/Al_2O_3 contains two forms of dispersed Re, three dimensional crystallites and a two dimensional phase which interacts strongly with the alumina surface. Calcination of Re/Al_2O_3 catalysts also leads to strong interactions between the alumina support and anionic species (e.g., ReO_4^-) involving Re^{4+} or Re^{7+} [6,14,45,46], Al–O–Re vibrations possibly having been detected in Raman spectra [14]. It is therefore proposed that raising the calcination temperature to 843 K promoted rhenium oxide–alumina interactions in a way which on reduction generated a new type of Re site, which was in close interaction with the alumina surface and provided a direct mechanism for the formation of $Re(CO)_3$ in the presence of CO. The initial $Re^{\bigcirc}$–CO band intensity was greater for catalyst which had been precalcined at the higher temperature in accordance with an enhanced dispersion and therefore, closer contact between Re and the alumina surface. A key factor in determining the product of adsorption might be the ease with which surface carbonyl complex species generated on the surface of Re aggregates can be transferred to anchoring sites [36,37] on alumina. The close proximity of Re adsorption sites and alumina would be expected to allow easy spillover of Re complexes including $Re(CO)_3$ from Re_x aggregates [35] across the Re/alumina interface. However, the growth of carbonyls on three dimensional Re particles without near-neighbour alumina sites may favour $Re_2(CO)_{10}$, which once formed may slowly transfer to the alumina surface but will not lose CO to form $Re(CO)_3$ without evacuation, thermal activation [35,37] or photolysis [36]. $Re_2(CO)_{10}$ ligates to Al^{3+} sites in alumina via a carbonyl oxygen atom [36]. $Re(CO)_3$ and $Re(CO)_5$ are more likely to be more strongly adsorbed via the formation of $\equiv Al$–O–$Re(CO)_x$ [36], or for $Re(CO)_3$ a complex involving three Al–O–Re bonds [35].

The spectrum in Fig. 5(c) is nearly identical to a reported spectrum for CO on Re/TiO_2 for which a full interpretation was not given [47] but which now appears to be primarily attributable to $Re(CO)_3$, showing that the CO induced disruption and reactions of Re to give carbonyl complexes also occur on a titania support.

The behaviour of CO towards Re in Pt–Re/Al_2O_3 was broadly the same as that for Re/Al_2O_3. Deconvolution showed that, apart from a shift in position of -9 cm^{-1} for $Re^{\bigcirc}$–CO, the positions and relative intensities of the bands due to Re carbonyls were similar for the Re and Pt–Re catalysts, confirming that the same species were formed. However, the band intensities were ca. 2.8 times bigger for Pt–Re(C) than for 0.3% Re/Al_2O_3 suggesting that a higher proportion of the Re was available for interaction with CO in Pt–Re than for Re alone. The result for Pt–Re(S) was between the other two. One explanation would be that Pt promotes the reduction of Re [10,24,25,27] thus providing more $Re^{\bigcirc}$ available for reaction. Chen et al. [46] also found that more $Re^{\bigcirc}$ was formed for Pt–Re than for Re alone. For Re alone, high temperature pretreatment before reduction leads to strong interactions between Re and the alumina surface [42–44] and Re involved in these interactions is difficult to reduce [14,35], even in the presence of Pt [16,17,27,44,46]. From one

study involving high temperature calcination followed by reduction it was concluded that Pt had no influence on the reduction of Re [15]. However, the final extent of reduction to Re° seems to depend on the precalcination temperature, higher temperature generating stronger Re–alumina interactions [45] and therefore, more difficult reduction, the reduction temperature, higher temperature favouring enhanced reduction [15,35], and Pt which promotes Re reduction. Here reduction of Re alone with the 763/893 pretreatments was probably not complete, but was promoted by the addition of Pt. However, it is highly unlikely [15,35] that the residual oxidised Re in Re/Al_2O_3 after the reduction treatment was sufficiently low to account for the enormous increase in Re–carbonyl band intensities for the Pt–Re catalysts. It is therefore concluded that Pt not only promotes Re reduction but also improves the dispersion of Re°.

The shift of -9 cm^{-1} for Re°–CO induced by Pt shows that the exposed Re° atoms must be influenced by Pt. A proposal that electron transfer occurs from Re to Pt [6] is not consistent with this result because enhanced cationic character of Re would shift the band in the opposite direction. A plausible explanation would be that dipolar coupling effects [7] for CO on Re sites are reduced by Pt implying that, although there is more Re on the surface in the mixed catalyst than for Re alone, smaller ensembles of Re atoms are available for CO adsorption. Charcosset et al. [27] concluded that exposed Re in $Pt–Re/Al_2O_3$ was on the surface of very small aggregates of Re or on the surface of Pt particles. The results for Pt–CO show that Re is not spread over Pt terraces, this conclusion also being consistent with the Re°–CO data. However, the decrease in coupling effects for CO on Re in Pt–Re would be in accordance with the existence of Re° atoms at kink or edge sites on Pt particles.

Peri [11] did not interpret his results for $Pt–Re/Al_2O_3$ in terms of the formation of $Re_2(CO)_{10}$ after the addition of CO although the spectra resembled the present results after short contact times. Here, longer contact times established that the behaviour of Re/Al_2O_3 in contact with CO [35] is replicated for the catalysts containing Re and Pt on alumina. Furthermore, the formation of $Re_2(CO)_{10}$ was promoted by Pt, and in accordance with the concurrent promotion of Re°–CO by Pt this may be attributed to the enhanced availability of exposed Re atoms for reaction with CO.

Calcination of Pt–Re catalysts leads to oxidised Re^{n+} species in intimate contact with the alumina support [44–46]. Reduction of these species may be difficult [16,17,27,44,46]. In reduced catalysts the Re component is also widely dispersed over the support [12,13], probably in very small Re aggregates [27]. As for Re/Al_2O_3 therefore, carbonylation of Re in Pt–Re catalysts can readily occur and leads to $Re_2(CO)_{10}$ ligated via carbonyl O-atoms to Al^{3+} sites on alumina [37], or subsequently to $Re(CO)_3$ which is chemisorbed on alumina via Re–O–Al bonding [35,36]. Existence of a proportion of the Re on the surface of Pt particles [27] may result from Pt-aided reduction of oxidised Re species [10,17,24,25,27], although the presence of Pt is not necessarily essential for complete reduction of Re [15,35]. However, if the Pt and Re behaved completely independently in these systems then the results for the interactions between CO and the Re component should be identical for Re alone and Pt–Re not only in kind but also in amount. The considerably enhanced Re–carbonyl amounts for Pt–Re show that the Pt and Re must be involved with each other either during the reduction process or in the subsequent attainment of equilibrium surface structures at the reduction temperature. The present results imply that if alloy formation takes place [6–10] then this is accompanied by Re segregation to particle surfaces without disrupting the integrity of arrays of Pt atoms in short terraces. High index or rough planes on three dimensional particle surfaces contain terraces consisting entirely of Pt with kink or edge sites at least in part occupied by Re. Although

these sites adsorbed CO to give Re°–CO, the question arises as to what extent they were involved in further reaction with CO to give multicarbonyls of Re. High temperature catalyst calcination/reduction, Fig. 10, caused sintering [41] of the reduced Pt which would have led to fewer kink and edge sites and therefore, less Re at these sites on the particle surfaces. This is consistent with the results for Pt–Re(C) for which less $Re_2(CO)_{10}$ was formed after the higher temperature treatments. However, for Pt–Re(S) the amounts of $Re_2(CO)_{10}$ formed were similar for the low and high temperature pretreatments suggesting an alternative precursor of the multicarbonyl species. The precursor was probably Re which was widely dispersed over the alumina surface [12,26]. An important influence of Pt on Re might therefore be that it favours two dimensional arrays of Re [26] over alumina rather than three dimensional Re particles. Thus Pt promotes overall Re dispersion and enhances the opportunity to generate carbonyl complexes from CO.

Calcination/reduction of Pt–Re/Al_2O_3 at 843/943 K enhanced the formation of $Re(CO)_3$ in accordance with the result for Re/Al_2O_3. Higher temperature calcination favoured a higher proportion of Re strongly interacting with the alumina surface via Re–O–Al bonds [14]. Isaacs and Petersen [48,49] showed that raising the pretreatment temperature before reduction decreased the migration of Re species across the alumina surface to Pt reduction centres. Here, the resulting Re species remaining dispersed on alumina after reduction were favourably disposed for reaction with CO to form $Re(CO)_3$, which was also immobilised on alumina via Re–O–Al bonding [35,36].

Calcination/reduction pretreatment temperatures were important in determining the relative behaviour of Pt–Re(C) and Pt–Re(S). After 763/893 K treatments the extent of formation of Re°–CO and $Re_2(CO)_{10}$ was greater for Pt–Re(C) than for Pt–Re(S). In contrast, after the 843/943 K treatments Pt–Re(S) gave more $Re_2(CO)_{10}$ and considerably more $Re(CO)_3$ than

Pt–Re(C). The latter in particular reflects high dispersion of a proportion of the Re over the alumina surface probably before as well as after interaction with CO. The distribution of Re over alumina is more favoured during very high temperature calcination and reduction for Pt–Re in which the Pt has been calcined before the addition of the Re precursor salt, rather than for coimpregnated Pt–Re. The addition of CO to Pt–Re(S) gave similar amounts of $Re_2(CO)_{10}$ after the low and high temperature treatments, Fig. 10. This complex probably results from reaction of CO with Re_x° aggregates [35] before migration onto the support [36,37]. The contrasting comparative behaviour of Pt–Re(C) and Pt–Re(S) after the two pretreatments must therefore be attributed to an effect primarily involving a marked reduction in $Re_2(CO)_{10}$ formation for Pt–Re(C) after the higher temperature treatments. Coimpregnation of Pt and Re at high temperature apparently reduced the availability of Re° sites. Possible contributions to this effect are improved alloying of Re° in composite particles, or, as observed from the Pt–CO data, sintering of Pt and therefore, fewer kink and edge sites on the Pt surfaces for Re° to occupy.

Carbon monoxide chemisorption has been used to assess metal area in supported Pt–Re catalysts [12]. The formation of multicarbonyl complexes and the time dependence of the interactions involving Re make CO adsorption experiments on mixed metal catalysts containing Re liable to error.

4.3. Catalyst coking

The high level of poisoning of CO adsorption at Pt sites in Pt/Al_2O_3 induced by heat treatment in heptane is consistent both with previous results for hydrocarbon–hydrogen reactions [50], and also with models in which carbonaceous deposits extending from kink and edge sites over Pt terraces [4] act as non-selective poisons, blocking Pt sites from CO. Similar results were reported from an infrared study of CO adsorp-

tion on Pt/Al_2O_3 which had been coked during the hydrogenolysis of hexane [51]. Heptane at 683 K would be expected to generate three dimensional carbon deposits, albeit with residual uncovered ensembles of Pt atoms [49]. The weak band due to adsorbed CO on Pt terraces after coking, Fig. 2(a), corresponds to CO molecules for which dipolar coupling [7] has been greatly reduced by coking of a high proportion of the terrace sites. However, a suggestion that adsorbed species may diffuse through the carbonaceous deposit [49] is borne out by the significant growth of the infrared band due to adsorbed CO with time, Fig. 2(c). CO promoted the partial removal of the blocking effect of carbonaceous deposits even at 293 K. Furthermore, the shift of the infrared band back towards higher wavenumbers shows that bigger aggregates of Pt atoms had become available rather than an increased number of the very small aggregates initially available after coking. Exposed ensembles of Pt atoms grew in size in the presence of CO which apparently promoted coke mobility [39,40], with possible clustering along steps and transference onto the alumina support [5]. The occurrence of the same effect for $Pt–Re/Al_2O_3$ adds further weight to the argument that Re was not dispersed on or in Pt terraces. The effect was slightly greater for Pt–Re(S) than Pt–Re(C) probably because double calcination of the Pt component in Pt–Re(S) induced sintering [41] and therefore a slightly greater number of terrace sites than in Pt–Re(C). In general the addition of Re decreased the coking of Pt in accordance with expectation, although the effect was not as great as in the presence of hydrogen which together with Re promotes coke removal [1–5,50].

Re alone was coked much less than Pt alone, but for Pt–Re the presence of Pt considerably enhanced the coking of Re. Either (a) exposed Re atoms were sufficiently influenced by adjacent or underlying Pt to catalyse enhanced coking, or (b) Re atoms generated by Pt-promoted reduction were more sensitive to coking than Re sites for Re alone, or (c) more likely, coke

formation on Pt was followed by transport not only onto the support [2,5] but also onto the Re. The greater degree of poisoning of Re° sites giving $Re_x^{\circ}–CO$ than of $Re_2(CO)_{10}$ formation for Re/Al_2O_3 suggests that $Re_2(CO)_{10}$ may not be derived only from Re_x crystallites [35]. A two dimensional Re phase interacting with the alumina surface [26] could also constitute a precursor of $Re_2(CO)_{10}$ complexes ligated to Al^{3+} cation sites [36]. The much greater level of coking of $Re^{\circ}–CO$ sites and $Re_2(CO)_{10}$ for Pt–Re than for Re alone shows that the poisoning effects of coke for Pt–Re affected Re sites not only at the surface of three dimensional particles (of Re alone [11–13] or Pt + Re [6–10]) but also in two dimensional arrays on alumina. Even if the latter were not associated with Pt atoms in the mixed catalyst [12], the general movement of coke [2,5,50] from Pt sites across the metal and support surfaces would account for the enhanced site poisoning. The enhanced coking for Pt–Re(C) compared with Pt–Re(S) suggests that there were stronger Pt–Re interactions in the coimpregnated catalyst and therefore a greater toxicity of coke [19].

Acknowledgements

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