FTIR study of CO adsorption on coked Pt–Sn/Al_2O_3 catalysts

Geomar J. Arteaga, James A. Anderson and Colin H. Rochester
Chemistry Department, Dundee University, Dundee DD1 4HN, UK

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Infrared spectra of adsorbed CO have been used as a probe to monitor changes in Pt site character induced by the coking of Pt/Al_2O_3 and Pt–Sn/Al_2O_3 catalysts by heat treatment in heptane/hydrogen. Four distinguishable types of Pt site for the linear adsorption of CO on Pt/Al_2O_3 were poisoned to different extents showing the heterogeneity of the exposed Pt atoms. The lowest coordination Pt atoms (ν(CO) < 2030 cm^{-1}) were unpoisoned whereas the highest coordination sites in large ensembles of Pt atoms (2080 cm^{-1}) were highly poisoned, as were sites of intermediate coordination (2030–2060 cm^{-1}). Sites in smaller two-dimensional ensembles of Pt atoms (2060–2065 cm^{-1}) were partially poisoned, as were sites for the adsorption of CO in a bridging configuration. The addition of Sn blocked the lowest coordination sites and destroyed large ensembles of Pt by a geometric dilution effect. The poisoning of other sites by coke was impeded by Sn, this effect being magnified for Cl-containing catalyst. Oxidation or oxychlorination of coked catalyst at 823 K followed by reduction completely removed coke from the catalyst surfaces.

Keywords: Pt–Sn/Al_2O_3, coking of, Pt–Sn/Al_2O_3, regeneration of after coking

1. Introduction

The deactivation by coking of Pt/Al_2O_3 hydrocarbon-reforming catalysts during use is hindered by the addition of Sn [1–7]. Pt–Sn/Al_2O_3 catalysts have greater stability because of the influence of Sn on coke deposition. Although Sn may not change the amount of coke formed, it can modify the nature of the coke deposited [8]. Three kinds of coke have been identified [9]. The presence of coke also changes catalyst selectivity, the effects being different for Pt and Pt–Sn [1,2,4]. Coke may block sites non-selectively [10], or be specifically formed at high- or low-coordination Pt sites [11], or can create new catalytically active sites [12]. Sn may favour the movement of coke from active sites onto the support [13] surface. Catalytic activity and selectivity are also dependent on Pt dispersion [14,15], which is influenced by the presence or absence of chlorine during catalyst preparation, and during catalyst regeneration by oxidation [16,17], which removes coke, or oxychlorination which removes coke and improves dispersion at least for Pt alone [18].

Bond has reviewed the role of carbon deposits in influencing the activity and selectivity of metal catalysts during hydrocarbon reactions [19]. Effects of coking on catalysis are only partly understood and further information on the effect of coke on the character of Pt sites is desirable. Infrared spectra of adsorbed CO have been used to probe changes in Pt site character in Pt/Al_2O_3 [16,18] and Pt–Sn/Al_2O_3 [20] catalysts after oxidation/reduction and oxychlorination/reduction cycles, and also the influence of coking on Pt–Re/Al_2O_3 catalysts after heat treatment in heptane [21]. This paper is concerned with using CO as a probe to monitor the effects of coking, by heptane/hydrogen reaction, of alumina-supported Pt and Pt–Sn catalysts in the presence and absence of Cl, and to assess the efficacy of oxidation/reduction or oxychlorination/reduction for catalyst regeneration after coking.

2. Experimental

Precursors of Pt(0.3%)–Sn(0, 0.15, 0.30 and 0.45%)/Al_2O_3 catalysts were prepared by impregnation of non-porous γ-alumina (surface area 110 $m^2\,g^{-1}$) with aqueous solutions of tetraammineplatinum(II) hydroxide and tin(II) oxalate, the latter being dissolved in aqueous nitric acid before mixing with the Pt salt and addition of the alumina. After evaporation to dryness the precursors were heated in air at 383 K for 15 h followed by CO_2-free dry air at 673 K for 1 h. After reduction the four catalysts contained mol Sn/mol Pt of 0, 0.82, 1.64 and 2.47.

Pressed discs of catalyst precursor (20 $mg\,cm^{-2}$) were mounted in a transmission cell and after appropriate treatments spectra at 4 cm^{-1} resolution were recorded, with the disc at ca. 293 K, using a Perkin–Elmer 1710 FTIR spectrometer.

Discs were subjected in various sequences to series of five different treatments, as follows:

(a) Calcination (designated calc) in flowing air, involving heating at 15 $K\,min^{-1}$ to 673 K and holding at 673 K for $1/2$ h, followed by reduction in flowing hydrogen at 673 K for 1 h.

(b) Oxidation (designated ox) in air (60 $ml\,min^{-1}$, 823 K, 1 h), followed by reduction as above.

(c) Oxychlorination (designated oxy), involving heating at 823 K for 1 h in flowing air containing 31 $\mu mol\,h^{-1}$ 1,2-dichloropropane per 50 mg of catalyst, followed by the standard reduction.

(d) Heat treatment (designated coke) at 623 K for 4 h in a hydrogen flow 25 $cm^3\,min^{-1}$ containing heptane with a mol C_7H_{16}/H_2 ratio of 1/11.5. Subsequent evacuation was started at 623 K (for 20 min) and continued during cooling to ca. 293 K.

(e) Exposure at ca. 293 K to six pressures of CO (designated CO) in the range 0.053 $N\,m^{-2}$ to 6.67 $kN\,m^{-2}$ followed by evacuation. Spectra were recorded at each stage of the experiment.

Sequences of treatment in each experiment are given in section 3. As an example, calc/ox/CO/coke/CO/oxy/CO/oxy/CO implies treatments as above all for the same disc in the sequence (a), (b), (e), (d), (e), (c), (e), (c), (e).

3. Results and discussion

Spectra of adsorbed CO are presented for the lowest and highest pressures studied, the latter with bands due to gas-phase CO subtracted out. Variations of band intensity with CO pressure gave estimates of the coverage of available Pt sites. Over all sites CO was more weakly adsorbed on coked rather than uncoked surfaces, the effect being greater for Pt alone than for Pt–Sn. At the lowest CO pressure the effect for Pt–Sn was either non-existent or reversed pointing to site heterogeneity.

3.1. Effects of coking on CO adsorption by Pt/Al_2O_3

Figure 1 compares spectra of adsorbed CO for catalysts which had been coked after calc, ox or oxy treatments with spectra for catalysts which had not been coked. At the lowest CO pressure the areas under the ν(CO) bands due to linearly adsorbed CO on coked catalysts were much weaker than those for the corresponding uncoked catalysts. The band maxima were shifted to lower wavenumbers suggesting that there was not simply non-selective site blockage by coke and retention of identical site character. The band envelopes for coked catalysts appeared within the corresponding envelopes for uncoked Pt suggesting that the shifts arose because Pt sites giving the higher wavenumber component (ca. 2042–2051 cm^{-1}) of the band envelopes were either selectively poisoned or subjected to a geometric or electronic effect of coke. Selective poisoning would be consistent with the conclusion [10,19] that low-coordination edge and corner atoms were more resistant to poisoning by coke deposition than higher-coordination Pt atoms. Lower band positions for ν(CO) may be correlated with decreasing Pt particle size [22] with the implication [23] that lower coordination of Pt atom sites leads to lower ν(CO). Electron transfer from adsorbed coke to Pt [2,24,25] would favour enhanced e-back donation from Pt to CO leading to a weaker C–O bond and, therefore, a possible contribution to the ν(CO) shift to lower wavenumbers. However, this electronic effect would also strengthen the Pt–CO bond which is contrary to the effect of coke on the band intensities as a function of CO pressure. Abon et al. [25] observed a weakening of the binding energy of CO on Pt(111) partly covered with carbon and attributed the effect to decreased 5σ to metal charge transfer for adsorbed CO. The inference of the present results is that there may have been an electronic effect of coke which weakened the Pt–CO bond [25], but that any effect of this on the ν(CO) band position was small. Work function measurements for coke deposits on Pt showed that e-transfer from coke to Pt can occur [24,25], although, in contrast, the absence of an electronic effect of coke on Pt sites has also been reported [10]. The dominant explanation of the results here is that Pt sites responsible for the ν(CO) band at 2042–2051 cm^{-1} were selectively poisoned by coke, but that sites giving the bands at $\nu(CO) < 2030$ cm^{-1} were not poisoned.

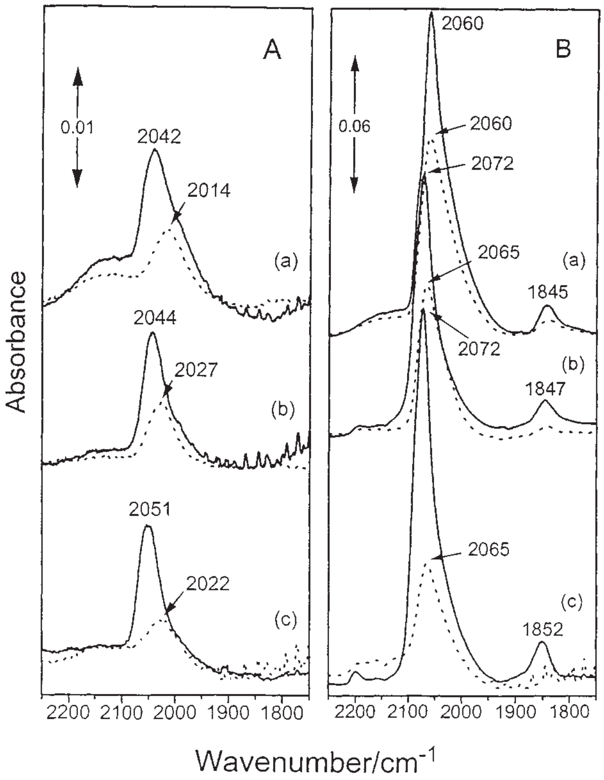

Figure 1. Spectra of Pt/Al_2O_3 plus CO at pressures of (A) 0.053 $N\,m^{-2}$ and (B) 6.67 $kN\,m^{-2}$. Full lines: (a) calc/CO, (b) calc/CO/ox/CO, and (c) calc/CO/oxy/CO. Dashed lines: (a) calc/coke/CO, (b) calc/coke/CO/ox/coke/CO, and (c) calc/coke/CO/ox/coke/CO/oxy/coke/CO.

At high coverages by CO of linear (2060–2065 cm^{-1}) and bridging (1845–1852 cm^{-1}) Pt sites in larger aggregates of exposed Pt atoms, partial blocking by coke also occurred, the effect being greatest for the oxychlorinated catalyst (figure 1(B)). The bands due to linear CO were at slightly lower wavenumbers for the coked catalysts after ox and oxy treatments than for uncoked catalysts. Again, an electronic effect of coke on Pt is unlikely to have been the major cause of this shift, which probably arose primarily from two factors. Firstly, the build up of surface coke will have reduced the average size of exposed Pt aggregates [8,10] and, hence, will have decreased the ν(CO) blue-shifting dipolar coupling interactions [26] between adjacent adsorbed CO molecules at high coverage. Secondly,

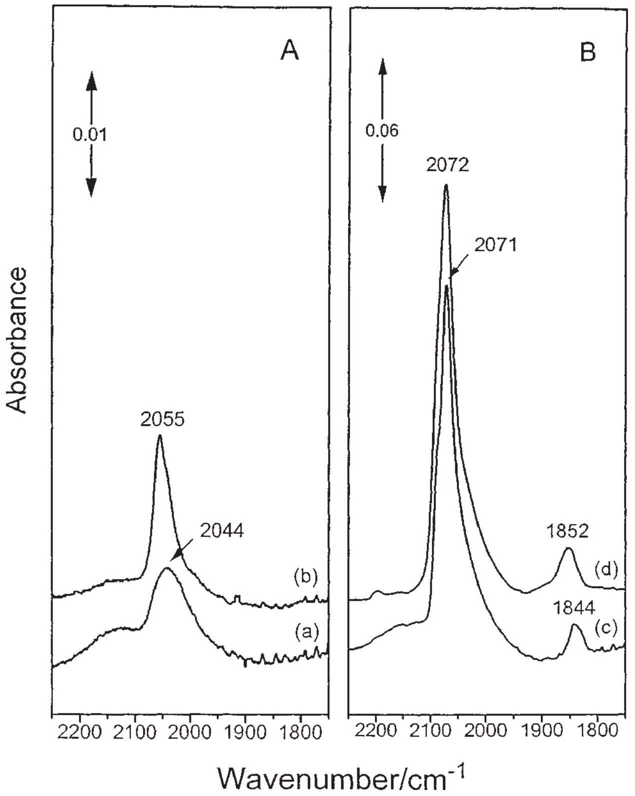

Figure 2. Spectra of Pt/Al_2O_3 plus CO at (A) 0.053 $N\,m^{-2}$ and (B) 6.67 $kN\,m^{-2}$. (a), (c) calc/coke/CO/ox/coke/CO/oxy/coke/CO/oxy/CO, and (b), (d) calc/CO/oxy/CO/oxy/CO.

selective site poisoning probably occurred. Particularly noticeable was the absence for the ox- and oxy-treated coked catalysts of the ν(CO) shoulder at ca. 2080 cm^{-1} due to CO adsorbed on the largest ensembles of Pt atoms present before coking. This supports conclusions that coke is preferentially retained on bigger ensembles with the structures of low index planes [1,2,8,10,11,13,19].

Figure 2 shows the results of experiments designed to test whether an oxy treatment after coking returned the catalyst to the same state as if no coking had occurred. One oxy treatment after coking gave, at high coverages of CO, ν(CO) bands due to both linear and bridged CO which were ca. 90% as intense as for catalyst without a history of coking. Furthermore, the dominant maximum had shifted back to 2071 cm^{-1} and the shoulder at 2080 cm^{-1} had returned. A single oxychlorination cycle after coking had largely restored the characteristics of uncoked catalyst. The comparison in figure 2 involved uncoked catalyst which had been subjected to two oxy cycles as the coked catalyst had also had two oxy treatments, but with coking between them. Results (figure 1(B), spectrum (c)) for uncoked catalyst after a single oxy cycle showed even closer agreement with the spectrum (c) in figure 2(B) suggesting that the removal of coke from Pt sites by a single oxy treatment was complete. In accordance with this result, Pieck et al. [17] reported that coke was removed from Pt/Al_2O_3 by oxidation above ca. 800 K.

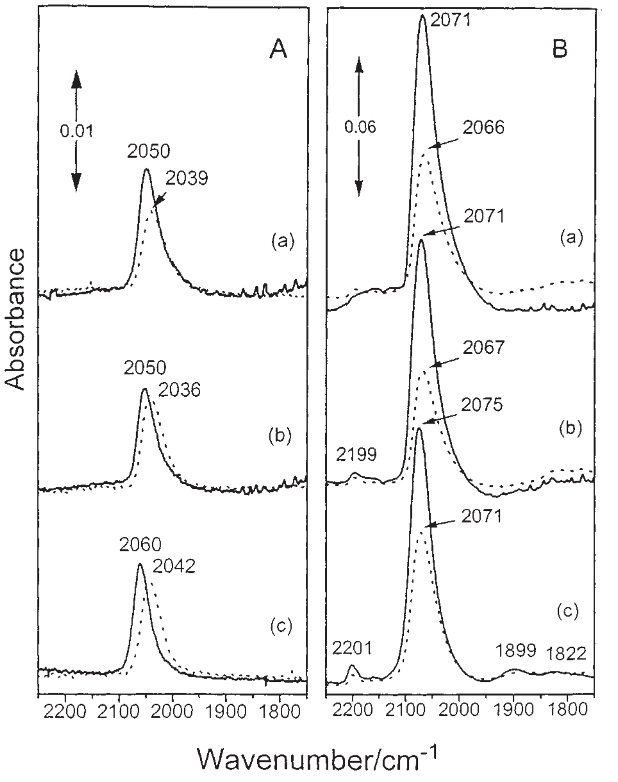

Figure 3. Spectra of Pt–Sn(0.45%)/Al_2O_3 plus CO at (A) 0.053 $N\,m^{-2}$ and (B) 6.67 $kN\,m^{-2}$. Full lines: (a) calc/CO, (b) calc/CO/ox/CO, and (c) calc/CO/ox/CO/ox/CO/ox/CO/ox/CO/ox/CO/ox/CO/oxy/CO/oxy/CO. Dashed lines: (a) calc/coke/CO, (b) calc/coke/CO/ox/coke/CO, and (c) calc/coke/CO/ox/coke/CO/oxy/coke/CO.

3.2. Effects of coking on CO adsorption by Pt–Sn(0.45%)/Al_2O_3

At low pressure of CO on Pt–Sn(0.45%)/Al_2O_3 (figure 3(A)) the intensity of the ν(CO) band due to linear CO was much less affected by coking than for Pt/Al_2O_3. Furthermore, the band shift was also much less, although for the ox and oxy catalysts the overall band envelope was not encompassed by the corresponding envelope for uncoked material suggesting that there was a small e-donating effect of coke on Pt [2,24,25] shifting the CO band to lower wavenumbers. This effect would also account for the slightly enhanced strength of adsorption of CO at low coverages induced by coking of Pt–Sn. However, the low coverage band positions for CO on coked Pt–Sn(0.45%)/Al_2O_3 were at significantly higher wavenumbers than the corresponding bands for Pt/Al_2O_3. The results confirm that low-coordination Pt sites (ν(CO) $<$ ca. 2030 cm^{-1}) were blocked by Sn before coking [22] and were therefore not available for occupancy by CO either before or after coking. The absence of the sites also apparently hindered the nucleation and growth of coke [10] on exposed Pt, although the smaller degree of coking in the presence of Sn may also reflect promotion by Sn of the movement of coke from the Pt to the alumina surface [1,3,9,13].

At higher CO pressures (figure 3(B)) more highly coordinated Pt sites (ν(CO) $>$ ca. 2060 cm^{-1}) were more poisoned by coke than were intermediate-coordination Pt sites (ν(CO) 2030–2060 cm^{-1}, figure 3(A)), further supporting the contention [11,19] that most of the coke on Pt blocked low Miller index, high-coordination Pt atoms. For Cl-free Pt and Pt–Sn(0.45%) catalysts the extents of coking of high-coordination sites were similar. However, after oxychlorination the Sn-containing catalyst was much more resistant to coking than Pt alone. Chlorine addition to Pt–Sn catalysts promotes either alloy formation [27,28], particularly at high percent Pt loading [29], or at least, for lower loaded catalysts, greater intimacy between dispersed Pt and Sn resulting in a reduction in the size of exposed ensembles of Pt atoms [20]. The conclusion that coking requires large ensembles of Pt atoms and that addition of Sn generates smaller ensembles which are less prone to coking [1,2,6,8,13,19] is therefore consistent with the infrared results, with the corollary that this effect is promoted by the addition of chlorine.

3.3. Effect of coking on CO adsorption by Pt–Sn(0.15%) and Pt–Sn(0.30%) on Al_2O_3

Figure 4 gives spectra for a single disc which was subjected to a consecutive series of treatments (figure 4, spectrum (c), dashed line) involving CO adsorption at six stages in the sequence. Spectra (a)–(c) compare results for CO adsorption before and after coking for the disc after calc, ox and oxy cycles, respectively. The results showed remarkable similarity to those in figure 3 supporting the validity of the conclusions for Pt–Sn(0.45%)/Al_2O_3, and showing that they were equally valid for catalysts containing 0.15% Sn. Even the band intensities for the catalysts were similar (figures 3 and 4) suggesting, in accordance with CO chemisorption data [20], that the transition from 0.15 to 0.45% Sn (mol Sn/mol Pt from 0.82 to 2.67) had at most only a small effect on the concentration and character of exposed Pt atoms. The low Sn loading was more than enough to effect changes in surface character from that for Pt/Al_2O_3, further additions of Sn apparently being segregated from the Pt presumably over the alumina support surface [30,31].

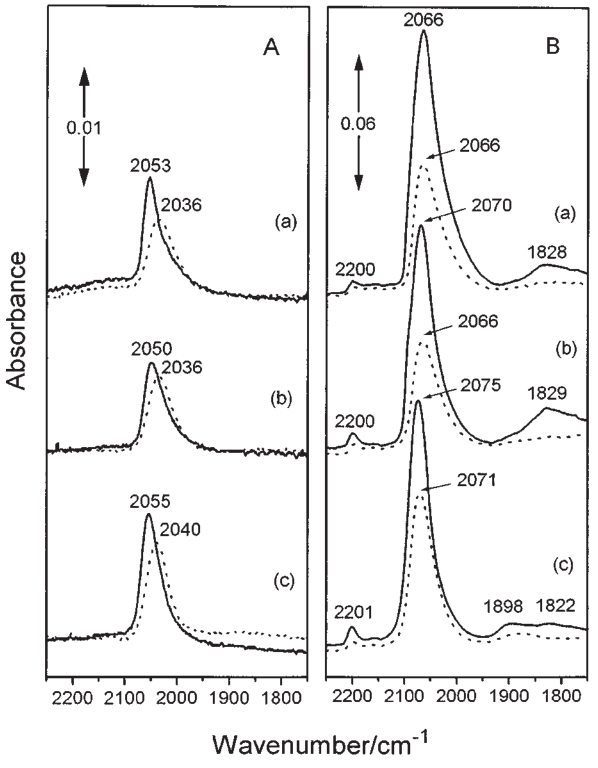

Figure 4. Spectra of Pt–Sn(0.15%)/Al_2O_3 plus CO at (A) 0.053 $N\,m^{-2}$ and (B) 6.67 $kN\,m^{-2}$. Full lines: (a) calc/CO, (b) calc/CO/coke/CO/ox/CO, and (c) calc/CO/coke/CO/ox/CO/coke/CO/oxy/CO. Dashed lines: (a) calc/CO/coke/CO, (b) calc/CO/coke/CO/ox/CO/coke/CO, and (c) calc/CO/coke/CO/ox/CO/coke/CO/oxy/CO/coke/CO.

The ability of an ox cycle or an oxy cycle to restore the catalyst after coking to its condition in the absence of coking was tested. The close similarity of the spectra (a) and (b) in figure 5 confirms for Pt–Sn/Al_2O_3, as for Pt/Al_2O_3 [17], that oxidation at 823 K is more than enough to remove coke from the Pt surface. As residual coke on the support after incomplete decoking may partially migrate back to the Pt surface during subsequent reduction and, therefore, block some of the Pt sites [17], the present results also indicate that coke removal from the support was probably complete after an ox cycle. This agrees with results for Pt and Pt–Re on alumina [17]. An oxy cycle also completely restored catalyst to its uncoked condition (figure 5(B), spectra (c) and (d)).

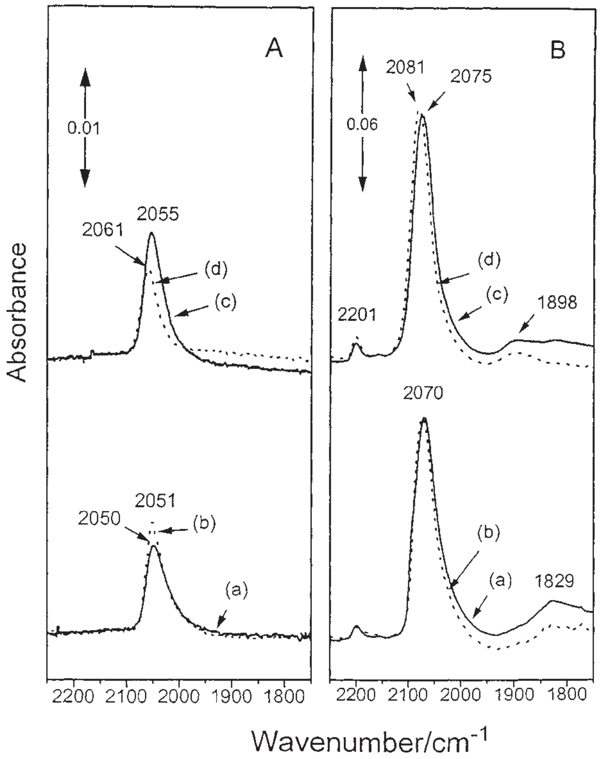

Figure 5. Spectra of Pt–Sn(0.15%)/Al_2O_3 plus CO at (A) 0.053 $N\,m^{-2}$ and (B) 6.67 $kN\,m^{-2}$. (a) calc/CO/coke/CO/ox/CO, (b) calc/CO/ox/CO, (c) calc/CO/coke/CO/ox/CO/coke/CO/oxy/CO, and (d) calc/CO/ox/CO/ox/CO/ox/CO/ox/CO/ox/CO/ox/CO/oxy/CO/oxy/CO.

3.4. Spectra of adsorbed coke

Figure 6 shows the changes in spectra induced by coking of Pt/Al_2O_3 after calc, ox and oxy treatments. A quartet of band maxima below 3000 cm^{-1} were of the general form characteristic of saturated hydrocarbon containing CH_3 (2959 and 2871 cm^{-1}) and CH_2 (2927 and 2852 cm^{-1}) groups, with relative intensities similar to those for heptane [32]. Evacuation after coking for 20 min at 623 K would have ensured that all weakly held heptane had been removed and, therefore, the results imply that residual strongly bonded alkyl species were present after coking. Further maxima at ca. 3058 cm^{-1} were characteristic of adsorbed unsaturated hydrocarbon species possibly of the type Pt=C=CH_2 or C_nH [33].

Addition of Sn in increasing amounts decreased the intensities of the ν(CH) bands which appeared after subsequent coking until for 0.45% Sn no bands were observed. For a 0.15% Sn content, only catalyst subjected to a calc cycle showed significant amounts of hydrocarbonaceous residue after coking. The decrease in hydrocarbonaceous material with increasing Sn content may reflect the Sn-promoted movement of coke from Pt sites to the support surface and a dominant graphitic character of coke on the support [1,3,9,13].

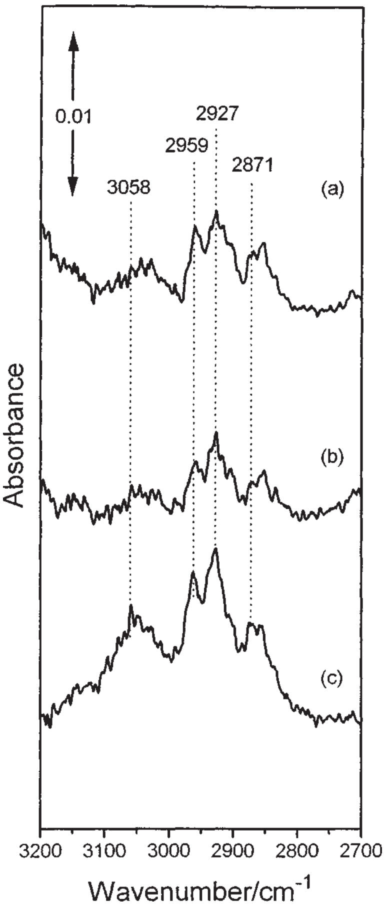

Figure 6. Spectra of Pt/Al_2O_3 after (a) calc/coke, (b) calc/coke/CO/ox/coke, and (c) calc/coke/CO/ox/coke/CO/oxy/coke.

4. Conclusions

The positions of ν(CO) bands due to linearly adsorbed CO on Pt are a function of Pt dispersion, highly dispersed Pt giving bands at lower wavenumbers than poorly dispersed Pt [22], the effect being related to the extent of coordination of exposed Pt atoms [23]. The present Pt/Al_2O_3 catalyst was apparently heterogeneous in this sense with four ranges of ν(CO) contributing to the overall band envelope but exhibiting distinguishably different behaviour on coking. The results are best summarised in terms of this distinction.

(a) $\nu(CO) < 2030$ cm^{-1}. The lowest coordination sites in Pt/Al_2O_3 apparently remained uncoked after heptane/H_2 treatment and evacuation at 623 K confirming [10] that these sites, which were probably corner or apex atoms on small Pt particles, were much more resistant to coking than all other types of Pt site present. This conclusion would be partly suspect if the loss of the bands at ca. 2044 cm^{-1} after coking eliminated intensity transfer [34] resulting in an enhanced contribution to the intensity of the bands at <2030 cm^{-1}. This would only happen if the two types of adsorption site were immediately adjacent to each other. The implication if this effect occurred here would be that some of the sites giving the bands at <2030 cm^{-1} were poisoned by coke. These sites were blocked by the addition of Sn [20,22] and did not contribute to the behaviour of Pt–Sn/Al_2O_3.

(b) $\nu(CO) = 2030$–2060 cm^{-1}. Intermediate coordination sites, possibly at edges or steps were heavily poisoned by coking in the absence of Sn suggesting that these may have constituted active sites for heptane decomposition [10] and also provided sufficient bonding opportunity [13,19] for adsorbed coke to remain at the sites in the presence of hydrogen. The addition of Sn considerably retarded the blocking of these sites by coke [8], possibly because the sites were partially blocked by Sn thereby reducing the ability of coke to multibond [5,8,13,19] to the surface. Furthermore, hydrocarbons bind more strongly to Pt/Al_2O_3 than Pt–Sn/Al_2O_3 [6,9] and, therefore, any hydrocarbonaceous residue formed at the sites in the presence of Sn may also be more labile and move to plane ensembles of Pt [11,19] or the support surface [9].

(c) $\nu(CO) = 2060$–2065 cm^{-1}. More highly coordinated Pt atoms in medium-sized ensembles of Pt atoms in Pt/Al_2O_3 were partially poisoned by coke which led to smaller ensembles of Pt atoms available for CO adsorption. Sn modified the sites in the same way as coke [8] and, therefore, the reduced size of ensembles for Pt–Sn/Al_2O_3 reduced the level of coking [1,2,13]. The opportunity for strong multibonding of coke to the Pt surface [13,19] would be reduced [5,8,10] by the geometric effect of Sn in reducing ensemble size. Enhanced intimacy between Pt and Sn was promoted by chlorine [20,26–28] which thereby increased the coke-inhibiting effect of Sn on Pt/Al_2O_3.

(d) ν(CO) = ca. 2080(sh) cm^{-1}. Large ensembles of Pt atoms akin to exposed low-index planes in Pt/Al_2O_3 were highly poisoned by coking in accordance with expectation [10,11,19]. The shoulder was also absent for Pt–Sn/Al_2O_3, further [8] illustrating a similarity between the effects of Sn and coke on Pt surface character. Sites for the adsorption of bridging CO were also at least partially poisoned by either Sn or coke.

(e) The clearly different effects of coking on the bands (a)–(d) due to adsorbed CO show that band maximum shifts for ν(CO) on the Pt/Al_2O_3 catalyst as a function of increasing CO pressure [20] were, at least in part, due to site heterogeneity, and could not be wholly attributed to shifts resulting from enhanced dipolar coupling interactions between adjacent CO molecules with increasing coverage. Site heterogeneity also accounted for the low-wavenumber tail in the ν(CO) band envelope at high coverages, and for the shoulder at 2080 cm^{-1} on the high-wavenumber side of the band maximum.

(f) ν(CH) = 2850–3100 cm^{-1}. In accordance with the present infrared band due to unsaturated CH species, Davis et al. [10] found that the chemical composition of CH species on Pt single-crystal surfaces after coking with a variety of alkanes was within the $1.0 < C/H < 1.6$ range. However, it also appears that some adsorbed hydrocarbon here retained alkane character and was therefore only anchored to Pt via one or two C adatoms in the heptane chain. Weaker ν(CH) bands for Pt–Sn catalysts conform with the inhibiting effect of Sn on coke formation on Pt sites [1,3], and with the expected lower H content of coke on the support [9,17] which is promoted by Sn. The coking of Pt/Al_2O_3 by heptane treatment in the absence of hydrogen gave much higher levels of poisoning of Pt sites than here, although subsequent exposure to CO gave a time-dependent decrease in the poisoning effect due to CO-induced coke mobility [21]. This effect was not apparent here because of reduced coking in the presence of hydrogen [13] which suppresses coke formation [9], inhibits C–metal multibonding [19], and causes rapid hydrogenolysis of dehydrogenation products of heptane on low-coordination Pt sites [19].

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