Journal of Catalysis **184,** 268–279 (1999)
Article ID jcat.1999.2433, available online at http://www.idealibrary.com on IDEAL®

Effects of Oxidation–Reduction and Oxychlorination–Reduction Cycles on CO Adsorption by Pt–Sn/Al_2O_3 Catalysts

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Received November 9, 1998; revised January 11, 1999; accepted January 13, 1999

Pt–Sn/Al_2O_3 catalysts containing 0.30 wt% Pt and 0, 0.15, 0.30, and 0.45 wt% Sn and prepared from Cl-free precursors have been studied by CO chemisorption and FTIR of adsorbed CO after each cycle in a series of six oxychlorination–reduction cycles or six oxidation–reduction cycles followed by oxychlorination–reduction. Spectra of CO on each catalyst directly after oxychlorination are also reported.

After oxychlorination catalysts contained exposed Pt sites present as Pt° (covered with O-adatoms), Pt(II), Pt(IV) oxide, $PtCl_2$ (forming $PtCl_2CO$ and $PtCl_2(CO)_2$ with CO), and PtO_xCl_y, the relative proportions of these species varying with Sn content. Tin hindered both catalyst sintering during oxidation and redispersion during oxychlorination. The IR results for oxidised catalyst after subsequent reduction were compatible with Pt° dispersed over a Sn(II)-modified alumina surface. However, addition of chlorine promoted greater intimacy between Pt and Sn with the latter blocking low coordination Pt sites and reducing the size of exposed ensembles of Pt atoms.

Two Pt(0.3%)–Sn(0.3%)/Al_2O_3 catalysts prepared from tin(II) oxalate and tin(II) tartrate gave different results emphasising the sensitivity of catalyst character to preparation procedure. © 1999 **Academic Press**

Key Words: **Pt–Sn/Al_2O_3, oxychlorination of; Pt–Sn/Al_2O_3, CO adsorption on.**

INTRODUCTION

Subjection of Pt/Al_2O_3 catalysts containing chlorine to a series of sequential oxidation–reduction cycles led to sintering of Pt when chlorine loss from the catalyst occurred (1). In contrast, the addition of chlorine in oxychlorination–reduction cycles was efficient in maintaining or improving Pt dispersion (2). Catalyst activity and selectivity in hexane reforming reactions were both influenced by sintering (3).

A significant effect on the catalytic behaviour of Pt/Al_2O_3 catalysts is also induced by the addition of tin (4–6). Studies of a high loading Pt(3%)–Sn(4.5%)/Al_2O_3 catalyst (7) have confirmed (8, 9) that the presence of chlorine favours the formation of Pt–Sn alloy rather than Pt° particles containing Sn atoms on the particle surfaces. Oxidation–reduction in the absence of chlorine generated Pt° with surface Sn, whereas oxychlorination–reduction under otherwise identical experimental conditions generated a Pt–Sn alloy, the latter exhibiting different catalytic behaviour than the former for heptane reforming reactions (7).

The present studies of CO chemisorption and of IR spectra of adsorbed CO on catalysts more akin to those used commercially for hydrocarbon reforming were therefore designed, as an extension of earlier studies of Pt/Al_2O_3 (1, 2), to explore the influence of added chlorine on the surface character of Pt–Sn/Al_2O_3 containing 0.3 wt% Pt and 0.15, 0.30, and 0.45 wt% Sn. The effects of oxychlorination at 823 K using a mixture of air and 1,2-dichloropropane prior to reduction are compared with the effects of oxidation under the same conditions but in the absence of 1,2-dichloropropane.

EXPERIMENTAL

A precursor of Pt(0.3 wt%)/Al_2O_3 catalyst was prepared by impregnation of a Degussa γ-alumina (surface area 110 m^2 g^{-1}) with aqueous tetraammine–platinum(II) hydroxide, evaporation to dryness, heating in air at 383 K for 15 h, and finally heating in dry CO_2-free air at 673 K for 1 h. Precursors of three Pt–Sn/Al_2O_3 catalysts containing 0.3 wt% Pt and 0.15, 0.30, and 0.45 wt% Sn (corresponding to mol Sn/mol Pt of 0.82, 1.64, and 2.47, respectively) were similarly prepared using tin(II) oxalate as the source of tin. Tin oxalate is insoluble in water and other common solvents, but was found to slowly (3 days) dissolve in aqueous nitric acid. Aqueous tetraammine–platinum(II) hydroxide was added to the resulting solution and the mixture was slurried with alumina before evaporation drying and heating in air as for Pt/Al_2O_3. A further catalyst containing 0.3 wt% Pt and 0.3 wt% Sn was also prepared using tin(II) tartrate as the source of tin. The preparation method was the same as that for the oxalate except that nitric acid was not added as the tartrate was sparingly soluble in water. Mixing the solutions containing Pt and Sn salts led to slight cloudiness and therefore addition to the alumina was carried out as quickly as possible. The catalysts with the same loadings prepared from the oxalate and tartrate salts

0021-9517/99 $30.00

are designated Pt–Sn(0.3%)/Al_2O_3(O) and Pt–Sn(0.3%)/Al_2O_3(T), respectively.

Transmission infrared spectra of pressed disks (20 mg cm^{-2}) of catalyst at ca. 293 K were recorded with a Perkin Elmer 1710 FTIR spectrometer at 4 cm^{-1} resolution. Pulsed chemisorption of CO on loosely powdered catalyst at ca. 293 K was measured using a Perkin Elmer AutoSystem XL gas chromatograph.

Catalyst disks in the infrared cell were initially subjected to a calcination–reduction cycle which involved calcination in air (heated at 15 K min^{-1} to 673 K and held at 673 K for 30 min) and reduction in flowing hydrogen (673 K, 1 h). Subsequent treatments involved either a series of six consecutive oxychlorination–reduction cycles each cycle consisting of oxychlorination (1 h at 823 K in a 60 ml min^{-1} flow of air containing 31 μmol h^{-1} 1,2-dichloropropane per 50 mg catalyst) followed by reduction in hydrogen (673 K, 1 h), or a series of six oxidation–reduction cycles each cycle consisting of oxidation in air (60 ml min^{-1}, 823 K, 1 h) and reduction in hydrogen (673 K, 1 h). Catalysts after six oxidation–reduction cycles were generally then subjected to one or two additional oxychlorination–reduction cycles. Spectra of adsorbed CO on reduced catalysts were recorded for seven CO pressures, corresponding to a range from low to complete coverage of Pt sites and after subsequent evacuation at ca. 293 K. In some experiments CO adsorption on oxychlorinated (unreduced) catalyst was studied.

Pulsed CO chemisorption was measured for Pt/Al_2O_3 (50 mg) and Pt–Sn/Al_2O_3 (150 mg) after each reduction stage in identical series of treatments to those used in the infrared experiments.

RESULTS

CO Adsorption on Reduced Catalysts

The infrared study of reduced catalysts generated far too many (ca. 650) spectra to be presented in detail here and therefore the following description of the results attempts to be brief and only emphasises major effects. Greater detail will be available elsewhere (10).

Figure 1 compares results for Pt alone and the highest Sn-loaded Pt–Sn catalyst at the highest CO pressure studied which gave complete coverage of Pt adsorption sites. Bands at 2060 and 1846 cm^{-1} for calcined–reduced Pt/Al_2O_3 were due to linear and bridged CO, respectively (11), and were at 2072 and 1847 cm^{-1} after the first oxidation–reduction cycle. The higher temperature oxidation had no effect on the subsequent generation of bridged sites, but the shift to a higher band position for CO on linear sites suggests that adsorption on "low-index" sites had become enhanced at the expense of adsorption involving step or kink sites (11), atomic Pt, or very small clusters of Pt atoms. Particle sintering might have partly caused this result since there was also a concomitant overall reduction in band intensity. A shoulder at 2080 cm^{-1} due to CO on a second type of low-index site after calcination–reduction was probably also present for the oxidised–reduced Pt/Al_2O_3, although in the latter case it was difficult to discern because of closer overlap with the dominant band maximum. However, this band appeared to be absent for calcined–reduced Pt–Sn(0.45%)/Al_2O_3 which gave a single maximum at 2071 cm^{-1} due to linear CO and no band due to bridged CO. The oxidised–reduced Pt–Sn catalyst gave nearly the same result although the band intensity was again weaker in accordance with slight sintering.

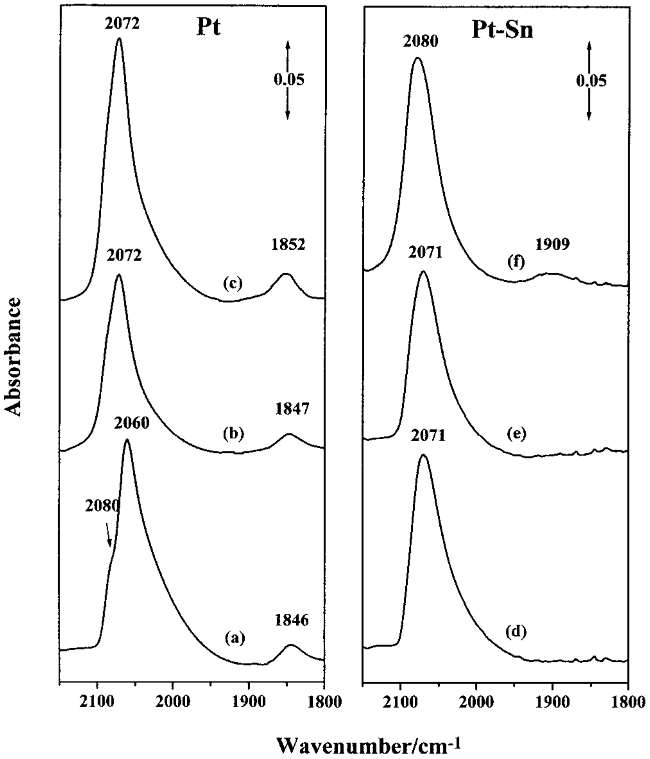


FIG. 1. Spectra, with gas-phase bands subtracted out, of (a)–(c) Pt/Al_2O_3 and (d)–(f) Pt–Sn(0.45%)/Al_2O_3 exposed to CO (6.67 kN m^{-2}) after (a), (d) calcination–reduction, (b), (e) the first oxidation–reduction cycle, and (c), (f) the first oxychlorination–reduction cycle.

One explanation for the absence of bridging Pt–Pt sites in the presence of Sn would be that Sn atoms were present on exposed Pt surfaces and at least blocked bridging sites. De La Cruz and Sheppard (11) ascribed a band at 1846 cm^{-1} for CO on Pt/SiO_2 to a two-fold bridged species on (111) surfaces or (111)-like terraces. Observation of a similar band here suggests an association with the surface of Pt particles as in Pt/SiO_2 rather than Pt atoms spread on alumina, although this conclusion is limited by the apparent insensitivity of the band position to the exact nature of the Pt surface (11). Dilution of arrays of exposed Pt atoms with Sn or interactions between Sn and Pt would also be expected to have geometric (12, 13) and/or electronic (14–19) effects on Pt atoms available for the linear adsorption of CO. For calcined–reduced catalyst the blue shift in the linear ν(CO) band position after adding Sn (Figs. 1(a) and (1d)) is the opposite of the corresponding effect for catalysts with a much higher Pt loading (7, 12, 13) for which dilution of surface Pt with Sn decreases dipolar coupling interactions between adjacent adsorbed CO molecules. It is therefore implied that the present result may be attributed at least partly to an electronic effect of Sn on Pt sites, the requirement being that the Sn decreases the electron density of exposed Pt atoms which hence give less e-back donation to CO for which ν(CO) is therefore higher. This proposal is consistent with the observation that Sn added to low-loaded Pt/Al_2O_3 catalysts induces a positive (blue) $\Delta\nu$(CO) shift due to electronic effects, but this is not observed for catalysts with a higher Pt loading (19). Schwank *et al.* (13) observed negative (red) shifts on adding Sn to Pt(1%)/Al_2O_3. Burch (5) argued that adding Sn to Pt/Al_2O_3 could either make the Pt electron deficient via interaction with Sn(II) ions on alumina or electron rich via formation of a solid solution of Sn in Pt. The former appears to be the case for the present catalysts containing 0.3 wt% Pt. In contrast, the ν(CO) band shift in the opposite direction on adding 4.5% Sn to Pt(3%)/Al_2O_3 may be attributed to dilution of exposed Pt atoms on Pt° particles by surface Sn° atoms (7). Under conditions of high Sn and Pt loadings, in the absence of chlorine (7), the Pt is mainly present as Pt° particles containing surface Sn, whereas at low Sn and Pt loadings dispersed Pt is in more intimate contact with the alumina surface which is also partly modified by Sn(II) cations (5, 8, 20–22). Despite this explanation involving a direct electronic effect of Sn on Pt there is also the possibility that the spreading of Sn over the alumina surface has an indirect effect favouring the partial aggregation of some of the Pt into Pt° particles which therefore give a band due to linearly adsorbed CO (Figs. 1(d) and 1(e)) similar to that for partially sintered Pt/Al_2O_3 after oxidation–reduction (Fig. 1(b)). With a low Sn loading the Sn will be well dispersed over the alumina surface and therefore probably only partially decorates the Pt particle surfaces. It is unlikely that a Pt–Sn alloy was formed in the absence of chlorine (7–9).

The band position effects of 0.15 and 0.30 wt% Sn at high coverages of CO after calcination–reduction or oxidation–reduction were similar to those for 0.45 wt% Sn. Band positions at low coverages (corresponding to a CO pressure of 0.053 N m^{-1}) were more difficult to measure accurately because upward shifts in band position with increasing coverage were particularly significant at very low coverages. This in part arose because the strongest adsorption sites gave CO bands which appeared first and remained with increasing coverage to contribute to spectra at high coverages as a low wavenumber tail on the main absorption bands. However, the shift in band maxima also arose from increasing dipolar coupling interactions between adjacent CO molecules as coverage of exposed arrays of Pt sites increased (11). All the sets of spectra here exhibited this effect as a function of CO pressure, the $\Delta\nu$(CO) shift for Pt–Sn catalysts being ca. 18–24 cm^{-1} with no obvious trends above experimental error as a function of Sn content or after calcination–reduction as opposed to oxidation–reduction. However, the shifts for oxidised–reduced Pt/Al_2O_3 after oxidation–reduction cycles were ca. 32 cm^{-1}, the bigger value reflecting a low coverage band position of ca. 2039 cm^{-1} as opposed to the value of ca. 2050 cm^{-1} for Pt–Sn catalysts. The latter could be due to an electronic effect of Sn on the most active Pt sites shifting the band to higher wavenumbers (19). However, a more plausible explanation would be that the strongest adsorption sites for CO on Pt/Al_2O_3 (2039 cm^{-1}) were inhibited by the presence of Sn, either via direct interactions of Sn with highly uncoordinated Pt atoms or via occupancy by Sn of sites on the alumina surface at which the Pt atoms were located. The significant $\Delta\nu$(CO) shifts with increasing coverage for Pt–Sn catalysts clearly show that, even though there may have been some Sn atoms on the Pt surfaces, exposed Pt atom sites for linear adsorption were sufficiently concentrated in the surface to allow dipolar coupling interactions between adjacent adsorbed CO molecules to occur. The dominant forms of Pt present in Cl-free Pt–Sn/Al_2O_3 after calcination–reduction and oxidation–reduction were therefore Pt° clusters or particles, with some surface Sn°, and Pt which was influenced electronically by oxidic Sn(II) cations spread over the alumina surface.

The band positions for linear CO on Pt/Al_2O_3 after oxychlorination–reduction were, as before (1, 2), similar to those after oxidation–reduction but with greater band intensities, confirming that chlorine favoured better Pt dispersion (Fig. 1(c)). The band due to bridge bonded CO was also more intense and was shifted slightly to 1852 cm^{-1}. For Pt–Sn/Al_2O_3 more significant changes occurred (Fig. 1(f)). For low coverages of CO and all Sn loadings the band due to linear CO was at 2059 ± 2 cm^{-1} and had shifted to 2079 ± 2 cm^{-1} at high coverage, these positions being consistent with shifts of ca. +8 cm^{-1} from the positions for oxidised–reduced catalyst. A band at 2060 cm^{-1} shifting to 2066 cm^{-1} with increasing coverage for Pt(3%)–Sn(4.5%)/Al_2O_3 was due to CO on Pt atoms diluted by Sn in the surface of particles of a Pt–Sn alloy (7). The present much higher band position at high coverage and the appreciably bigger band shift with increasing coverage suggest that the formation of Pt–Sn alloy particles could not be primarily responsible for the results. The results are more consistent with the existence of small arrays of Pt atoms in clusters adjacent to the Sn-modified alumina surface and influenced by the e-withdrawing effects of Cl-adatoms which are retained in the catalyst after reduction (23). Meitzner *et al.* (24) concluded for a Pt(1.1%)–Sn(1.2%)/Al_2O_3 catalyst containing chlorine that the Pt was largely dispersed as Pt clusters on alumina which had Sn^{2+} present at the surface. In contrast bimetallic clusters were formed for Pt–Sn/SiO_2 (24). A band at ca. 1900 ± 10 cm^{-1} for all the Pt–Sn/Al_2O_3 catalysts after

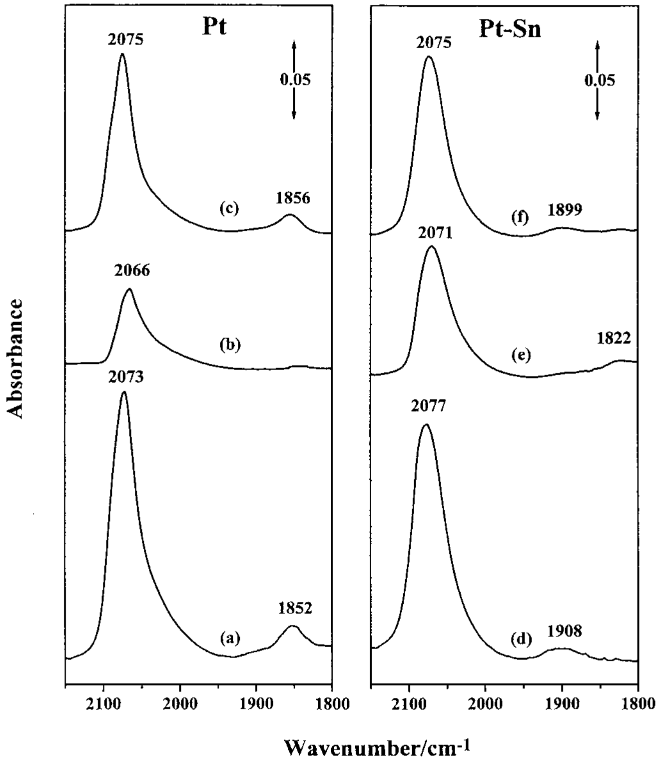


FIG. 2. Spectra, with gas-phase bands subtracted out, of (a)–(c) Pt/Al_2O_3 and (d)–(f) Pt–Sn(0.45%)/Al_2O_3 exposed to CO (6.67 kN m^{-2}) after (a), (d) the sixth oxychlorination–reduction cycle, (b), (e) the sixth oxidation–reduction cycle, and (c), (f) the second oxychlorination–reduction cycle following six oxidation–reduction cycles.

oxychlorination–reduction (Fig. 1(f)) was never present after oxidation–reduction and is unusually high for bridged CO on Pt catalysts (11, 25). This too is tentatively ascribed to the influence of Cl-adatoms on ν(CO) for Pt_2CO involving adjacent pairs of reduced Pt atoms which have been rendered cationic by e-withdrawal. There was a slight hint (Fig. 2(a)) of the band for Pt/Al_2O_3 after oxychlorination–reduction, but the appearance of a clear maximum apparently depended on a synergistic effect involving both Sn and Cl.

Comparison of Figs. 1 and 2 shows the effects of repeated oxidation–reduction or oxychlorination–reduction cycles on CO adsorption. In the presence of chlorine the spectra for both Pt/Al_2O_3 and Pt–Sn/Al_2O_3 were insensitive to repeated cycles. Both the band intensities and their positions were hardly affected by up to six cycles which was the maximum consecutive number studied. In contrast, although band positions remained about the same, in the absence of chlorine the bands due to adsorbed CO became progressively weaker with each successive cycle particularly for Pt/Al_2O_3. The results for Pt/Al_2O_3 were consistent with earlier contrasts between the effects of oxidation (1) and oxychlorination (2) prior to reduction. Addition of Sn induced partial resistance to Pt sintering in the absence of chlorine. However, the sintering effects of oxidation–reduction cycles were reversed by subsequent oxychlorination–reduction cycles for both Pt/Al_2O_3 and Pt–Sn/Al_2O_3 (Figs. 2(c) and 2(f)). Band intensities were partially restored and the band positions became more characteristic of the Cl-containing catalyst.

Band intensities, measured as the total areas under the band envelopes due to linearly adsorbed CO, are compared in Fig. 3 with the CO chemisorption results. Neither sets of data give completely reliable indications of comparative numbers of exposed Pt atoms because the comparisons ignore other modes of CO adsorption than Pt–CO on Pt, adsorption on alumina, and differences between extinction coefficients of bands contributing to the band envelopes. However, the infrared and chemisorption results broadly show parallel behaviour. Previous studies of Pt/Al_2O_3 involved catalysts which already had a Cl-content before being subjected to oxidation–reduction cycles and showed that, depending on oxidation temperature, successive cycles initially improved Pt dispersion but progressive loss of chlorine eventually led to decreases in dispersion (1, 2). The latter effect occurred even after the first cycle for the present Pt/Al_2O_3 catalyst which contained no chlorine, and further cycles led to progressive decreases in dispersion. Oxychlorination–reduction cycles, however, maintained a good level of dispersion which was independent of the number of cycles carried out. The CO/Pt data showed that after six oxidation–reduction cycles subsequent oxychlorination and reduction regenerated the good dispersion characteristic of Cl-containing catalyst. The infrared data exhibited the same trend although the two sets of results only showed qualitative agreement. A similar discrepancy has been observed and discussed before (2) and also existed here for Pt–Sn.

The CO/Pt values for Pt–Sn/Al_2O_3 were closely similar after oxidation–reduction and oxychlorination–reduction treatments and only showed slight trends (worse dispersion after oxidation–reduction, better after oxychlorination/reduction) which were dependent on the number of cycles (Fig. 3). Furthermore, oxychlorination–reduction after six oxidation–reduction cycles had little effect on dispersion. Results for the other Pt–Sn/Al_2O_3(O) catalysts were the same. The infrared intensities showed somewhat bigger variations but confirmed that losses of dispersion induced by high temperature oxidation followed by reduction were considerably less for Pt–Sn/Al_2O_3 than for Pt/Al_2O_3. In general Sn addition decreased Pt dispersion. For Pt alone, and the 0.15, 0.30, and 0.45% Sn catalysts, the CO/Pt values after calcination–reduction were 0.49, 0.36, 0.31, and 0.32, respectively. Raising the heat treatment temperature in air from 673 K (calcination) to 823 K (oxidation) in the first cycle decreased these values to 0.46, 0.29, 0.26, and 0.26, respectively. After the sixth oxidation cycle the values had been

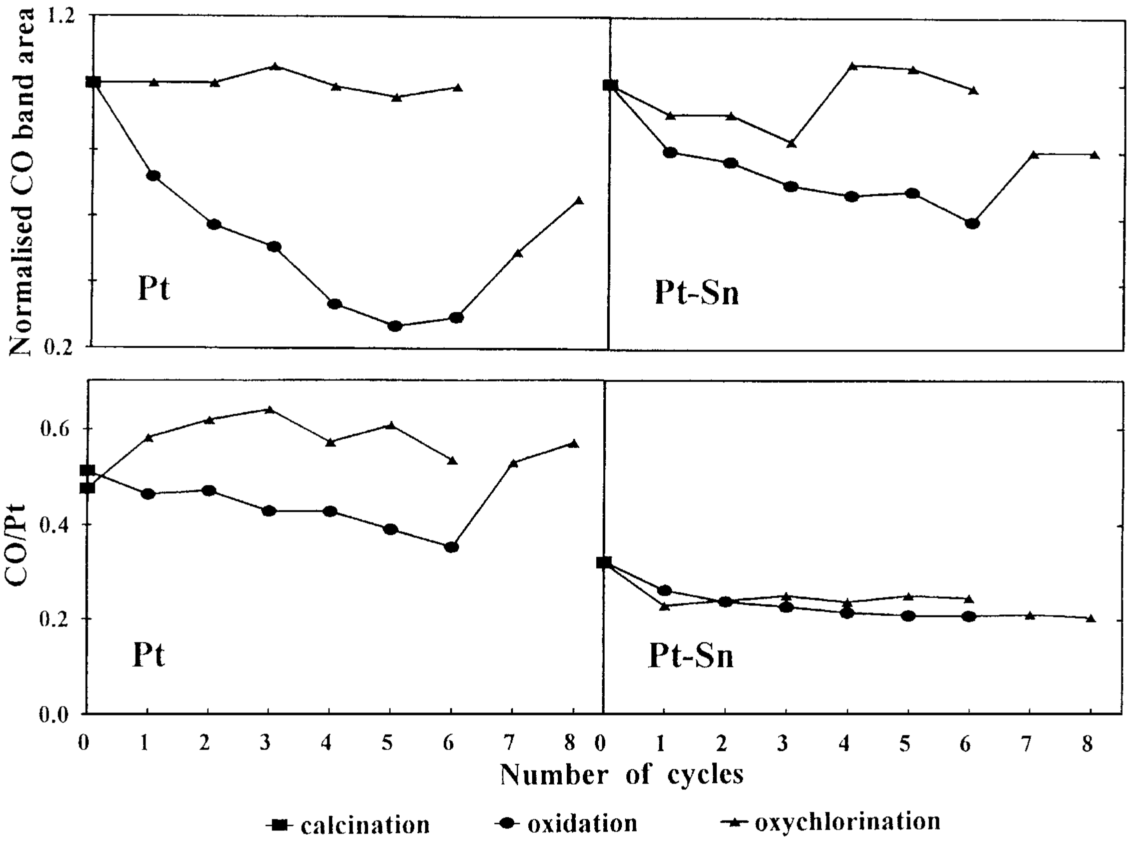


FIG. 3. Normalised CO band areas and CO/Pt values for Pt/Al_2O_3 and Pt–Sn(0.45%)/Al_2O_3 after calcination–reduction, oxidation–reduction cycles, and oxychlorination–reduction cycles.

further decreased to 0.35, 0.22, 0.21, and 0.21, respectively, but after two subsequent oxychlorination cycles became 0.57, 0.24, 0.23, and 0.21, respectively. The latter values resembled those of 0.58, 0.23, 0.24, and 0.23 for the four catalysts after a first oxychlorination cycle immediately following calcination–reduction. The addition of Sn to Pt/Al_2O_3 greatly decreased the magnitude of dispersion changes associated with oxidation or oxychlorination treatments followed by reduction, although changing the Sn content from 0.15 to 0.45% had comparatively little additional effect. The CO/Pt values after six oxychlorination–reduction cycles were 0.53, 0.24, 0.26, and 0.25, respectively.

CO Adsorption on Oxychlorinated Catalysts

CO was adsorbed on catalysts after oxychlorination in an attempt to gain information about catalyst structure before reduction. Figure 4 shows the spectra for Pt/Al_2O_3. A shoulder at 2099 cm^{-1} is ascribed to CO linearly adsorbed at Pt atoms on a surface covered with O-adatoms (11). This constituted the strongest mode of adsorption, the band appearing at low CO pressures. As the pressure was increased a band which appeared at 2118 cm^{-1} was due to CO on PtO_2 (26), and two further bands at 2162 and 2142 cm^{-1} are typical of chloro-complexes of platinum containing ligated CO (2, 27–29). A band at 2145 cm^{-1} for Pt/Al_2O_3 treated with CCl_4 in the absence of oxygen was ascribed by Melchor *et al.* (27) to a $PtCl_2CO$ surface complex. The molecular complex $(Cl_2PtCO)_2$ gives a ν(CO) band at 2146 cm^{-1}, and $Cl_2Pt(CO)_2$ gives bands at 2162 and 2200 cm^{-1} (28, 29). A weak band here at 2200 cm^{-1} was just detectable at moderate surface coverages (Fig. 4(c)) or after evacuation (Fig. 4(f)), but was obscured at high CO pressures by a strong band at 2200 cm^{-1} (Fig. 4(e)) due to weakly adsorbed CO ligated to Al^{3+} sites in the alumina surface (29). At the highest CO pressures two further bands became prominent at 2172 and 2133 cm^{-1}. These were not observed by Melchor *et al.* (27) suggesting that their presence here was associated with the addition of oxygen during the chlorination treatment. They are therefore assigned to CO ligated to two surface oxychloro–platinum complexes, or, as the bands apparently grew together, a single gem–dicarbonyl at a Pt site also ligated to both oxygen and chlorine atoms. A strong maximum at 2135 cm^{-1} and a weaker band at 2172 cm^{-1} for Pt(3%)–Sn(4.5%)/Al_2O_3 have previously been attributed to CO interacting with PtO_xCl_y spread over the alumina support surface (7). A broad band at ca. 1800 cm^{-1} for CO on oxychlorinated Pt/Al_2O_3 (Fig. 4) was greatly weakened on evacuation and was due to adsorption on the alumina support (30, 31).

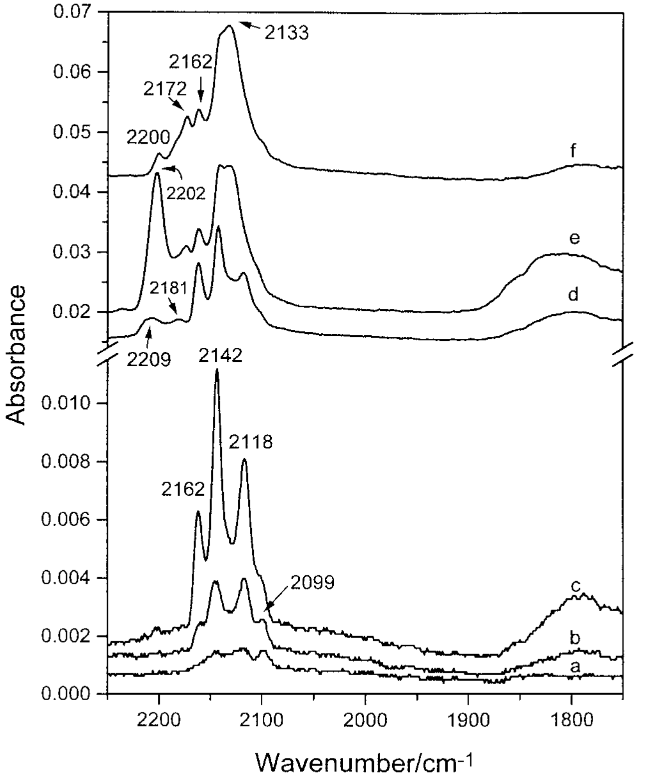


FIG. 4. Spectra of oxychlorinated Pt/Al$_2$O$_3$ exposed to CO at pressures of (a) 0.053, (b) 0.107, (c) 0.533, and (d) 133 N m^{-2}, (e) 6.67 kN m^{-2} (gas subtracted), and (f) after susequent evacuation.

In contrast to the results for Pt/Al$_2$O$_3$, spectra of Pt–Sn(0.15%)/Al$_2$O$_3$ exposed to CO after oxychlorination were dominated by a band at 2092–2105 cm^{-1} (Fig. 5) due to CO linearly adsorbed on Pt° surfaces covered with O-adatoms (11). Apart from a band at 2131 cm^{-1}, which itself was ca. 50% weaker than for Pt/Al$_2$O$_3$, all the bands due to CO interacting with chloro–Pt and oxychloro–Pt complexes were extremely weak. The concomitant extreme weakness of the band at ca. 1800 cm^{-1} suggests a blocking effect of Sn which would have been spread over the alumina surface (5, 8, 20, 21, 32). The spreading of Sn not only prevented CO adsorption on alumina, but also severely hindered the spreading (2, 33, 34) of Pt complexes over the alumina surface.

The relative intensities of the bands due to CO interacting with Pt, PtO$_2$, chloro–Pt, and oxychloro–Pt complexes varied with the Sn content of the catalyst (Figs. 4–7). After the large increase in intensity of the band at ca. 2100 cm^{-1}, due to CO on a Pt° surface with O-adatoms, caused by adding 0.15% Sn, the band remained at about the same intensity for all three oxalate-derived catalysts containing Sn, although with a slightly higher value for 0.3% Sn than for 0.15 or 0.45% Sn. The decrease in intensity of the band at 2118 cm^{-1}, due to CO on PtO$_2$, caused by 0.15% Sn was progressively reversed by the addition of more Sn, the band being about the same intensity for 0.45% Sn as for Pt alone. The weakening effect of 0.15% Sn on maxima at ca. 2143 and 2162 cm^{-1}, ascribed to CO interacting with chloro–Pt complexes, was also slightly reversed by a 0.3% Sn content, although the small enhancement was not increased for 0.45% Sn for which the band at 2162 cm^{-1} was almost absent. Additional Sn apparently prevented the generation of chloro–Pt sites at which two CO molecules could adsorb to form a gem–dicarbonyl complex. In contrast, and in parallel with the result for CO on PtO$_2$, the 50% loss in intensity of the band at ca. 2130 cm^{-1} due to CO interacting with oxychloro–Pt species was progressively reversed with the addition of more Sn, the intensity for 0.45% Sn being about the same as that for Pt alone. A band at ca. 2177 cm^{-1}, which is a typical position for CO adsorbed at Pt(II) sites (35), was only detectable as a weak shoulder for Pt alone but was increasingly prominent with increasing Sn content. The band at ca. 1800 cm^{-1} due to adsorption on alumina was partially restored for catalysts containing 0.45% Sn suggesting that the blocking effect on surface sites on alumina by tin had been removed to some extent. The implication that a different form of tin was present may be correlated with proof from X-ray diffraction that crystallites of SnO$_2$ were present in the much higher loaded catalyst Pt(3%)–Sn(4.5%)/Al$_2$O$_3$ after an identical oxychlorination treatment to that used here (7).

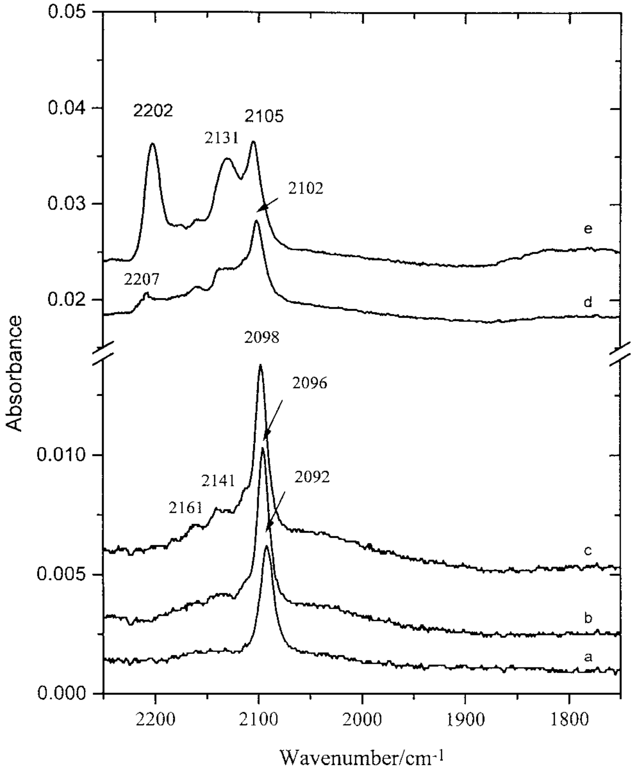


FIG. 5. Spectra of oxychlorinated Pt–Sn(0.15%)/Al$_2$O$_3$ exposed to CO at pressures of (a) 0.053, (b) 0.107, (c) 0.533, and (d) 133 N m^{-2} and (e) 6.67 kN m^{-2} (gas subtracted).

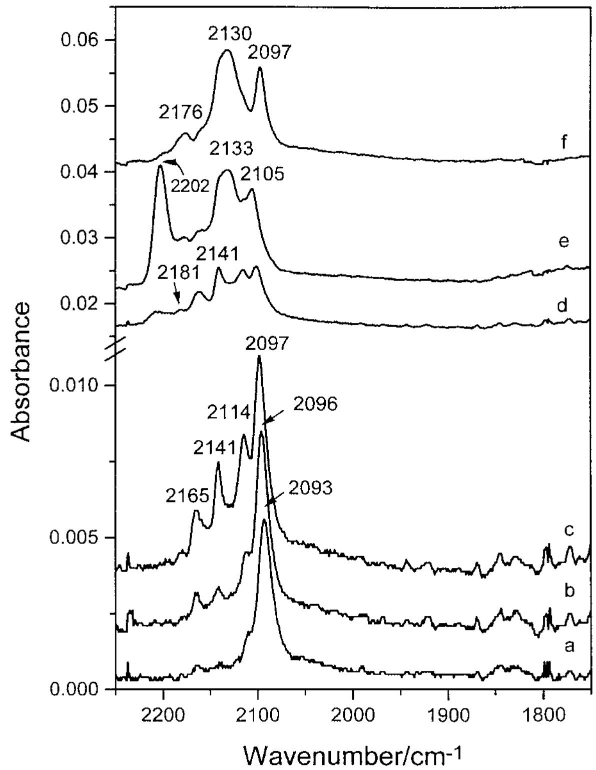


FIG. 6. Spectra of oxychlorinated Pt–Sn(0.3%)/Al_2O_3(O) exposed to CO at pressures of (a) 0.053, (b) 0.107, (c) 0.533, and (d) 133 N m^{-2}, (e) 6.67 kN m^{-2} (gas subtracted), and (f) after subsequent evacuation.

Spectra of CO on oxychlorinated catalysts during the sequences of successive cycles were occasionally recorded and were consistent with the figured spectra for a first oxychlorination. One important result involved CO adsorption on Pt–Sn(0.45%)/Al_2O_3 which had been subjected to calcination–reduction followed by six oxidation–reduction cycles and one oxychlorination–reduction cycle before oxychlorination and exposure to CO. The resulting spectra were identical to those in Fig. 7 showing that the reactivity and mobility of species present during oxychlorination treatments ensured a common end result no matter what was the past history of the sample.

Results for Pt–Sn(0.3%)/Al_2O_3(T)

Results for the 0.3% Sn-containing catalyst prepared from tin(II) tartrate were sufficiently different from those for the equivalent catalyst prepared from tin(II) oxalate to illustrate the sensitivity of catalyst behaviour to preparation procedure. The value of CO/Pt for the (T) catalyst after calcination–reduction (0.11) was much less than that (0.36) for the (O) catalyst. The partial precipitation during mixing of solutions of the Sn and Pt salts before addition to alumina led to a dried (T) precursor which after calcination at 673 K differed in character from the (O) precursor after the same treatment. In contrast, heat treatment in air at 823 K (oxidation) largely removed the difference in behaviour, CO/Pt for the (T) catalyst being in the range 0.18–0.22 (Fig. 8) after each of six oxidation–reduction cycles compared with 0.20–0.26 for the (O) catalyst. However, subsequent oxychlorination–reduction generated a much better dispersed (T) catalyst (CO/Pt 0.32) than did the (O) catalyst (0.19). Furthermore, a sequence of six oxychlorination–reduction cycles gave CO/Pt values in the ranges 0.26–0.34 (Fig. 8) for the (T) catalyst and 0.24–0.26 for the (O) catalyst. The consistently better Pt dispersion in the (T) catalyst than in the (O) catalyst after oxychlorination–reduction reflects, but to a lesser extent, the effect of this treatment on the dispersion of Pt in Pt/Al_2O_3 suggesting that a proportion of Pt in the (T) catalyst was not influenced by the presence of Sn.

The normalised band areas from infrared spectra of adsorbed CO (Fig. 8) confirmed the conclusions from the CO/Pt data. As for the (O) catalyst the proportional variations in the absorbance areas were greater than the variations in CO/Pt. However, the trends in absorbance and CO/Pt behaviour were similar. As oxychlorination had a

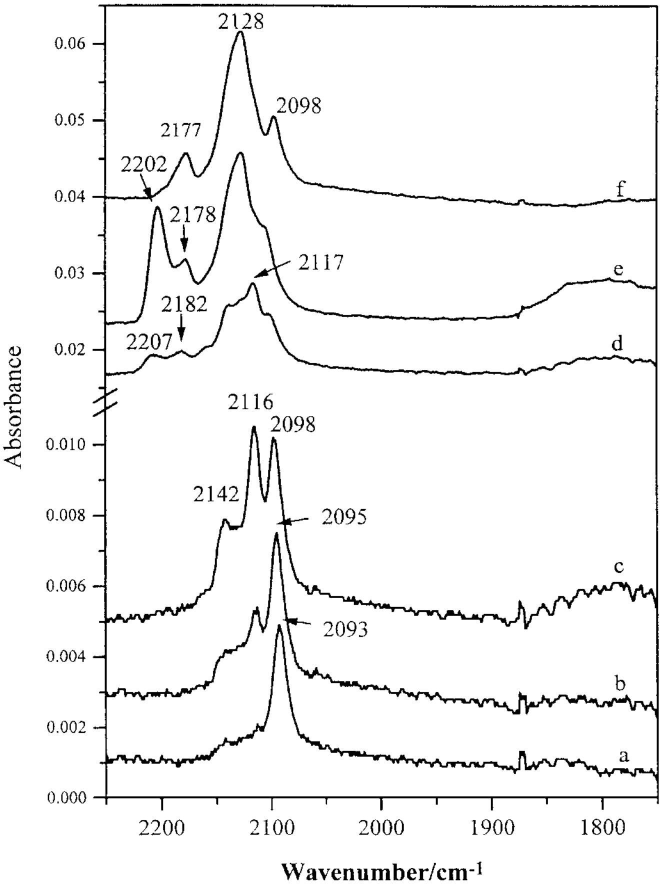


FIG. 7. Spectra of oxychlorinated Pt–Sn(0.45%)/Al_2O_3 exposed to CO at pressures of (a) 0.053, (b) 0.107, (c) 0.533, and (d) 133 N m^{-2}, (e) 6.67 kN m^{-2} (gas subtracted), and (f) after subsequent evacuation.

much bigger enhancing effect on dispersion for the (T) catalyst than for the (O) catalyst, particularly clear (Fig. 8) was the effect of oxychlorination after six oxidation–reduction cycles in returning the reduced (T) catalyst to the high level of dispersion also induced by oxychlorination–reduction cycles directly after calcination–reduction.

Spectra of the oxychlorinated (T) catalyst exposed to low CO pressures resembled the result for Pt alone in that the band at 2099 cm^{-1} was almost absent (Fig. 9). Furthermore, a band at 2116 cm^{-1}, showing the presence of PtO_2, was about the same intensity as for Pt alone and more intense than for the Pt–Sn(0.3%)/Al_2O_3(O) catalyst, the latter also showing a prominent bant at ca. 2096 cm^{-1}. However, the similarity between the results for the two catalysts involved the appearance of bands at 2145 and 2160 cm^{-1} for low CO pressures, and at 2176 and 2130 cm^{-1} after contact with a high pressure followed by evacuation. After evacuation the spectrum of the (T) catalyst, as for Pt/Al_2O_3 but in contrast to the (O) catalyst, exhibited no band at 2097 cm^{-1}. The infrared results therefore support the suggestion that, although the (T) and (O) catalysts show broadly similar behaviour, the (T) catalyst also exhibits some characteristics which are more typical of Pt in the absence of Sn. Spectra of CO on the (T) catalyst after calcination–reduction, two oxychlorination–reduction cycles, and then oxychlorination and exposure to CO were nearly identical to the results in Fig. 9 showing that repeated oxychlorination–reduction cycles did not alter the results.

Spectra of CO on the reduced Pt–Sn(0.3%)/Al_2O_3(T) catalyst confirmed that the major difference from the other catalysts occurred after calcination–reduction when the band positions (e.g., 2077 cm^{-1} for high CO pressure) for linearly adsorbed CO were at ca. 6–15 cm^{-1} higher wavenumber than for any of the samples made from tin(II) oxalate or for Pt alone. The bands are more suggestive of low-index crystal planes of platinum (11) in accordance with the low CO/Pt value indicative of catalyst sintering. The overall band intensity was also much less for the (T) catalyst rather than the (O) catalyst which is also consistent with sintering. However, exposure to CO after oxidation–reduction gave bands in positions (2071–2074 cm^{-1}) which were similar to those for the other catalysts confirming that higher temperature oxidation at least partially removed the discrepancy between catalyst structure and behaviour. Band positions after oxychlorination–reduction and exposure to CO were not discernibly different for the (T) and (O) catalysts containing 0.3% Sn. However, the band intensities for the (T) catalyst were much higher than those for the (O) catalyst in accordance with the CO/Pt chemisorption data.

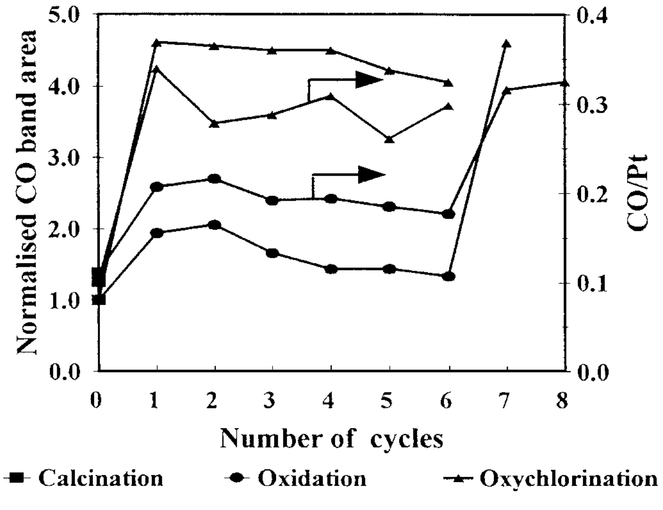


FIG. 8. Normalised CO band areas and CO/Pt values for Pt–Sn(0.3%)/Al_2O_3(T) after calcination–reduction, oxidation–reduction cycles, and oxychlorination–reduction cycles.

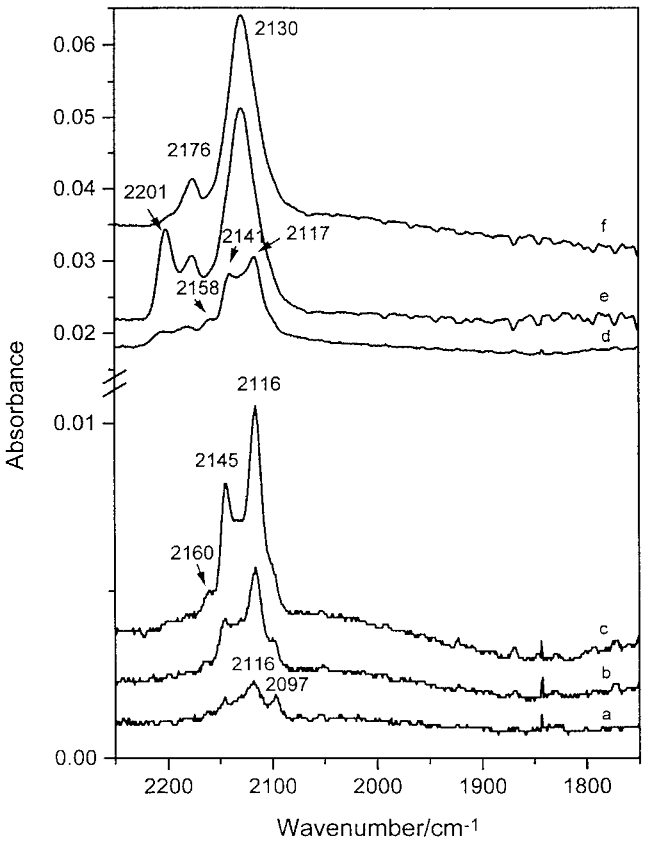


FIG. 9. Spectra of oxychlorinated Pt–Sn(0.3%)/Al_2O_3(T) exposed to CO at pressures of (a) 0.053, (b) 0.107, (c) 0.533, and (d) 133 N m^{-2}, (e) 6.67 kN m^{-2} (gas subtracted), and (f) after subsequent evacuation.

DISCUSSION

Effect of Cl on Reduced Pt/Al_2O_3

The complete absence of chlorine from the initial Pt/Al_2O_3 catalyst led to an immediate loss of dispersion after oxidation at 823 K followed by reduction. The previous catalyst, which initially contained 1.27% Cl, underwent an increase in dispersion after oxidation at 723, 793, 843, or 893 K followed by reduction, the increase being bigger the higher was the oxidation temperature (1). The difference between the results for the two catalysts confirms (1, 2) that the generation of an improved dispersion after each cycle was directly related to the Cl-content of the catalyst. Loss of chlorine during repeated oxidation–reduction cycles eventually leads to a worsening of the Pt dispersion (1, 2), this effect being inhibited by replacing the oxidation steps by high-temperature oxychlorination involving either oxygen/carbon tetrachloride (2) or air/1,2-dichloropropane.

Oxychlorinated Pt/Al_2O_3

Previous spectra of oxychlorinated Pt(0.3%)/Al_2O_3 exposed to CO gave a strong maximum at 2139 cm^{-1} and a weaker band at 2198 cm^{-1} (2). Both of these features were present here (Fig. 4(f)) although the former maximum was composed of contributions from two bands at 2142 and 2133 cm^{-1}. The present spectra have provided more information about the state of the Pt in the oxychlorinated catalyst before reduction. The bands at 2099 cm^{-1}, due to Pt° particles with O-adatoms (11), and 2118 cm^{-1}, due to PtO_2 (26), were not identified before, nor were they observed by Melchor *et al.* (26) for Pt/Al_2O_3 which had been heated at 473 or 573 K in an argon–carbon tetrachloride mixture. The latter treatment did, however, give maxima at 2145 cm^{-1}, ascribed to a surface $PtCl_2CO$ complex, and at 2160 and 2195 cm^{-1}, ascribed to $PtCl_2(CO)_2$ (26, 28, 29). Chlorination in CCl_4 at 573 K caused significant loss of Pt from the catalyst via the formation of a volatile $PtCl_2$–$2AlCl_3$ complex (26). In contrast, X-ray fluorescence analyses of catalysts identical to those used here showed that the present oxychlorination procedure gave no loss of Pt (36). Oxychlorination did generate surface chloro–Pt(II) species which interacted with CO to give bands at 2142, 2162, and 2200 cm^{-1} (Fig. 4(c)). However, the additional bands at 2133 and 2172 cm^{-1}, due to oxychloro–Pt surface complexes, did not appear for the chlorinated catalyst (26) and provide a mechanism for the stronger bonding of Pt to the alumina support surface during oxychlorination (33, 34) rather than chlorination (26). Chlorination of Pt/Al_2O_3 before reduction leads to sintered Pt (26), whereas the formation of mobile oxychloro–Pt complexes during oxychlorination favours spreading over the alumina surface and hence an improved dispersion after reduction (33, 34). The addition of oxygen during oxychlorination before exposure to CO also led to the presence of the additional bands due to Pt(IV)–oxidic (2118 cm^{-1}) and Pt(II)–oxidic (ca. 2181 cm^{-1}) species, both probably in intimate contact with the alumina surface, and Pt° (2099 cm^{-1}) which would have been formed by the decomposition of PtO_2 at 823 K even in an air atmosphere. Oxidation or oxychlorination of Pt(3%)–Sn(4.5%)/Al_2O_3 at 823 K under identical conditions to those here gave a catalyst with a powder X-ray diffraction pattern characteristic of Pt° crystallites and not PtO_2, although infrared spectra of adsorbed CO showed that the latter was also present (7). Here, the identity of the infrared band shapes and positions for oxidised–reduced and oxychlorinated–reduced Pt/Al_2O_3 exposed to CO shows that the Pt was in the same form after the two treatments. The better dispersion after oxychlorination–reduction must be associated with the spreading of chloro–Pt and particularly oxychloro–Pt complexes over alumina during oxychlorination and the subsequent decomposition of the complexes to smaller aggregates of Pt atoms during reduction.

Reduced Cl-free Pt–Sn/Al_2O_3

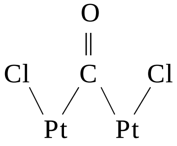
The Sn in Pt–Sn/Al_2O_3 catalysts exists as either Sn° (which may be alloyed (19, 20, 22, 23, 37, 38) or in a solid solution (5, 15) with Pt°, or it may exist in the surface of arrays or particles containing Pt° (7, 19)) or as oxidic Sn, predominantly Sn(II), spread over the alumina surface (5, 13, 20, 21, 37, 39). Similarly for Pt the formation of alloys or solid solutions with Sn° may be accompanied or replaced by clusters of Pt° atoms (7) or forms of Pt which may be atomic (40, 41) or very small (42) in intimate contact with alumina or Sn(II)-covered alumina (5, 19, 21, 24). Discussion usually centres around the dominant alternatives of a Pt–Sn 1 : 1 alloy or Pt/SnO_x/Al_2O_3, which represents Pt spread over a Sn-modified alumina surface (19). However, Pt° particles rather than alloy may also be present for a Cl-free catalyst even in the presence of excess Sn (7). The conclusion from the present results for Cl-free catalysts after calcination–reduction or oxidation–reduction that at least some of the Pt was electron deficient through e-donation to Sn(II) is consistent with the presence of dispersed Pt over Sn-modified alumina (5, 15). Intimate contact between Pt° and Sn° in alloy or solid solution would be expected to give an opposite electronic effect involving e-donation from Sn to Pt (5, 14, 17). The present conclusion is also consistent with XRD evidence that the Cl-free catalyst containing ten times the loadings of both Sn(4.5%) and Pt(3%) to those used here did not, after exactly the same treatments, contain any Pt–Sn alloy, the Pt being predominantly present as Pt^0 particles partially decorated by Sn° atoms (7). The Pt–Sn alloy in Pt–Sn/Al_2O_3 is strongly disrupted by oxidation treatment (38). Even for the Pt–Sn/SiO_2 catalyst, for which alloy formation is favourable, oxidation–reduction treatments may cause partial disruption of the alloy and formation of unalloyed surface Pt (9). The propensity for alloy formation in the Pt–Sn/Al_2O_3 catalyst increases with increasing Sn/Pt atomic ratio (22, 37), although in one study (40) reduced Sn could not be detected for Sn/Pt ratios less than two. The present data for the ratios of 0.82 (0.15% Sn) and 1.64 (0.3% Sn) are consistent with this conclusion. For the higher ratio of 2.47 (0.45% Sn) the infrared results resembled those for the lower Sn loadings and therefore compelling evidence for the presence of a 1 : 1 Pt°–Sn° alloy was absent.

The big decrease in CO uptake for the Cl-free catalyst on adding 0.15% Sn to Pt/Al_2O_3 is consistent with a similar effect on H_2 adsorption. A proposal that the presence of Sn gives fewer adjacent Pt sites for H_2 dissociative adsorption (43) is in accordance with the disappearance of bridging sites for CO adsorption on Cl-free catalysts, an effect which has been reported before (16). However, the increasing dipolar coupling interactions between adjacent CO molecules with increasing coverage show that arrays of adjacent Pt atoms must have remained present but favoured adsorption of CO in a linear configuration. Schwank *et al.* (13) concluded for similar catalysts that Pt was present in monometallic form with some particles in intimate contact with ionic Sn. The distribution of Pt in an oxidised catalyst may partly involve stronger interactions between Pt and the Sn-modified alumina surface than between Pt and unmodified alumina and partly involve Pt^0 particles or PtO_2 decorated with oxidic tin. Either possibility would explain why Sn hindered Pt sintering during oxidation–reduction cycles. This contrasts with the effect of oxychlorination in promoting spreading of mobile chloro–Pt and oxychloro–Pt complexes over Sn-free alumina and with the effect of oxidation of Sn-free Pt/Al_2O_3 in the absence of chlorine in promoting aggregation of Pt at 823 K to form Pt° particles even in air. The influence of Sn in hindering changes in catalyst dispersion induced by oxidative preatreatments was also apparent during oxychlorination.

Reduced Cl-Containing Pt–Sn/Al$_2$O$_3$

Powder XRD analysis of the present Pt–Sn(0.45%)/Al_2O_3 catalyst after oxychlorination–reduction showed no evidence for detectably large crystallites of Pt° or Pt–Sn 1 : 1 alloy. This shows that the Pt was present only as small clusters or particles. The beneficial effect of chlorine on alloy formation (7–9) apparently becomes less significant when the Sn loading is small (8, 22, 23, 37–40, 44) and the majority of the Sn exists in the ionic Sn(II) state dispersed on alumina (8, 42). Other reports also suggest that alloy is not usually a major component of low-loaded Cl-containing catalysts (5, 13, 20, 39). However, the catalytic behaviour of low-loaded catalysts has recently been interpreted (41) in terms of effects involving the generation of Pt–Sn alloy (38) or a solid solution of Sn in Pt. Alloy has been detected by XRD in catalysts containing the somewhat higher Pt loadings than that here, 0.5% (38) or 0.6% Pt (23). Lieske and Völter (8) proposed for catalysts containing 0.6 and 1.2% Pt that the majority of the Sn in reduced catalyst was present as Sn(II) on alumina, but that a small amount of Sn formed Pt°–Sn° alloy clusters on alumina surrounded by surface stabilised Sn(II) species. The formation of such clusters would be consistent with the present infrared band position shifts for adsorbed CO (blue shift in $\Delta\nu$(CO) in going from Pt to Pt–Sn if the exposed Pt atoms in Pt°–Sn° were more influenced by the e-withdrawing effects of oxidic Sn(II) (5, 15) and possibly chlorine (blue shift of $\Delta\nu$(CO)) than the e-donating effect (5, 14, 17) of Sn° (red shift) combined with the removal of dipolar coupling effects for adsorbed CO (12, 13) induced by dilution of the Pt cluster surfaces by Sn (red shift). The blue shift in $\Delta\nu$(CO) with increasing surface coverage for oxychlorinated–reduced $Pt–Sn/Al_2O_3$ argues against the extreme geometric effect induced by 1 : 1 Pt°–Sn° alloy formation in which individual exposed Pt atoms were surrounded by Sn°. However, a comparison of ν(CO) band shapes for all the present Pt–Sn catalysts after reduction shows that the low wavenumber tail was nearly absent from spectra after oxychlorination–reduction and that the band at low coverages was at higher wavenumber for the Cl-containing catalyst than for the Cl-free catalyst. This suggests that high energy low-coordination Pt sites were covered with Sn (45) for the former more than the latter. A model consistent with the present results would involve small arrays of exposed Pt atoms on mats or particles interacting with the Sn(II) oxide–modified alumina surface, the exposed Pt atoms being influenced by the electronic effect of Cl atoms and a geometric blocking effect of low coordination sites by Sn. This model does not propose a 1 : 1 Pt°–Sn° alloy is formed, but acknowledges that Cl promotes intimacy between Sn (Sn(II)O and Sn°) and Pt on the alumina surface. Hobson *et al.* (39) reported that intermetallic Pt°–Sn° species were formed if the reduction temperature exceeded 700 K, which is above the 673 K used here.

The band at ca. 1900 cm^{-1} for oxychlorinated–reduced $Pt–Sn/Al_2O_3$ catalyst is tentatively ascribed to a bridging CO species the complex



existing on small clusters of Pt which were bonded to alumina via interactions involving a few Pt atoms probably in the vicinity of Sn(II) cations (24). Pt atoms at the edge of clusters or in monolayer arrays of Pt may be linked to the alumina surface by Pt–O–Sn^{2+} bonds (46) and hence will have a tendency towards cationic character, which will favour retention of Cl at the sites thus providing a synergistic e-withdrawing effect of Sn and Cl on the Pt atoms. A significant blue shift in the $\Delta\nu$(CO) band position for the bridged CO species will therefore result. Although chlorine is retained by the catalyst during reduction there is evidence that some of the chlorine associated with alumina after oxidation of a Cl-containing catalyst moves elsewhere (23) and a possibility is that some Cl-adatoms exist on Pt° surfaces. The present oxychlorination treatment involved exposing catalysts to an excess of Cl (Cl/Pt ratio of 80/1) which probably favoured this possibility.

Oxychlorinated Pt–Sn/Al_2O_3

The addition of 0.15% Sn to Pt/Al_2O_3 greatly reduced the generation of chloro–Pt complexes during oxychlorination and decreased the formation of oxychloro–Pt complexes by ca. 50%. Spreading of oxidic tin over alumina hindered the stabilising influence of the alumina surface on these complexes. The consequence was that after reduction the Sn-containing catalyst contained less well dispersed Pt. The generation of oxidic Pt(IV) species during oxychlorination was largely inhibited, suggesting that for oxychlorinated Pt/Al_2O_3 these species too were in intimate contact with and stabilised by the alumina, but that this was also hindered by Sn oxide. The formation of significant amounts of Pt° during oxychlorination of Pt–Sn/Al_2O_3 at 823 K is consistent with infrared results for a much more highly loaded catalyst (7).

The effects of 0.3 and 0.45% Sn on the species present after oxychlorination partly reversed the effects of the initial addition of 0.15% Sn. A significant result for 0.45% Sn was the partial restoration of the band at ca. 1800 cm^{-1} due to adsorption on the alumina support (30, 31). Increased Sn loading apparently favoured an alternative form of Sn, probably crystallites of SnO_2 which have been shown to exist in oxychlorinated (7) and chlorinated (20) Pt–Sn/Al_2O_3 and hence re-released some of the alumina surface which became available for interaction with oxychloro–Pt and oxidic Pt(IV) species. The bands due to CO at Pt(IV) oxide and PtO_xCl_y sites were of about the same intensities for Pt–Sn(0.45%)/Al_2O_3 as for Pt/Al_2O_3. A logical corollary would be that the CO/Pt value for the oxychlorinated–reduced catalyst, which fell from 0.58 to 0.23 on addition of 0.15% Sn, should also be restored to about the same value as that for Pt/Al_2O_3. This did not happen suggesting that the subsequent reduction stage re-established coverage of alumina by Sn(II) which prevented the beneficial effects of oxychloro–Pt complexes on catalyst dispersion. Results for a high-loading Pt–Sn/Al_2O_3 catalyst have shown that crystallites of SnO_2 generated during oxychlorination are destroyed by subsequent reduction confirming the mobility of Sn species under reduction conditions (7). The results for oxychlorinated catalysts do not preclude the possibility that some surface species contained fully ligated Pt atoms which were not available for interaction with adsorbed CO and would not therefore be detectable by infrared study of CO adsorption.

Effect of Catalyst Precursor Salt

The differences between the results for Pt–Sn(0.3%)/Al_2O_3(T) and Pt–Sn(0.3%)/Al_2O_3(O) further emphasise the sensitivity of catalyst character to the method of preparation (9, 21, 37, 38, 42). In particular the sequence of mixing the alumina, Pt, and Sn components is important (9, 21, 37, 42). For example, co-impregnation of alumina with Pt and Sn may lead to a high level of Pt–Sn interaction (9, 37), whereas sequential impregnation of Pt followed by Sn (9) or of Sn followed by Pt (21) results in a large amount of separated Pt. The precipitation which occurred here on mixing solutions of tin(II) tartrate and tetraammineplatinum(II) hydroxide would be expected to impair intimate mixing of the Pt and Sn components during the subsequent impregnation onto alumina and is therefore likely, in accordance with the observed results, to favour enhanced separation of Pt and Sn. The ν(CO) band positions and intensities and the reduced CO uptakes for calcined/reduced Pt–Sn/Al_2O_3(T) were all consistent with larger Pt° particles than in the oxalate-derived catalyst, although the difference became less significant after oxidation–reduction, where the higher oxidation temperature would have promoted mobility of component species and assisted towards partial attainment of the same end result after subsequent reduction. Furthermore, oxychlorination–reduction gave the Pt–Sn(0.3%)/Al_2O_3 catalyst for which the infrared band intensities and the CO/Pt values were intermediate between those for Pt–Sn(0.3%)/Al_2O_3(O) and Pt/Al_2O_3 in accordance with the presence of a high proportion of Pt which was not influenced by Sn. The spectra of CO on the oxychlorinated (T)-catalyst also exhibited characteristics typical of Pt/Al_2O_3, in particular only a weak band due to Pt° with O-adatoms and a stronger band than for the (O)-catalyst due to oxidic Pt(IV). PtO_2 is a relatively immobile species compared with PtO_xCl_y (8) and therefore may favour the formation of Sn-free Pt° on reduction.

ACKNOWLEDGMENTS

We thank the Consejo Nacional de Investigaciones Cientificas y Tecnologicas, Venezuela, and the University of Zulia, Venezuela, for a studentship, the Royal Society (London) for a University Research Fellowship, and Dr. S. M. Becker for XRD analyses.

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