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

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Infrared spectra of CO adsorbed on Pt–Re/Al_2O_3 after individual steps in sequences of oxidation, oxychlorination, and reduction treatments are compared with corresponding spectra for Pt/Al_2O_3 and Re/Al_2O_3, and with H_2 chemisorption data. Chloro-Pt and oxychloro-Pt complexes were formed independently of the presence of Re during oxychlorination and contributed to a Cl-dependent enhanced dispersion of Pt in Pt–Re/Al_2O_3. After a given treatment the dispersions of Pt in Pt/Al_2O_3 and Pt–Re/Al_2O_3 were similar, but the H_2 uptakes were considerably decreased by the addition of Re. In general, reduced Pt–Re/Al_2O_3 contained very small bimetallic particles with Re surface enrichment. Small ensembles of high coordination Pt^0 atoms were retained, although Re atoms may have been located at both ensemble and edge sites. Surface sintering after repeated oxidation/reduction cycles led to an enhanced coverage of bimetallic particles by Re, the effect being reversed by oxychlorination/reduction cycles. © 2000 Academic Press

INTRODUCTION

The losses of activity resulting from the sintering and coking of Pt/Al_2O_3 catalysts during use in catalytic hydrocarbon reforming reactions are conventionally restored by a regeneration process involving oxychlorination followed by reduction. Infrared studies of CO adsorption on highly dispersed oxide-supported metal catalysts have been widely used to probe metal site character and the geometric and electronic effects of surface modifiers or second metallic components on the catalytically active metal. Studies of Pt/Al_2O_3 after series of oxidation/reduction and oxychlorination/reduction treatments have confirmed that the presence of chlorine during regeneration is essential for the formation of well-dispersed Pt (1–3), giving high catalytic activity (4, 5). The effects of regeneration procedures on CO adsorption have also been studied for Pt–Sn/Al_2O_3 (3) and Pt–Ge/Al_2O_3 (6) catalysts. However, there have been no such studies for Pt-Re/Al_2O_3 which, after sulphur treatment, is widely used in hydrocarbon reforming catalysis. The present work was, therefore, aimed at remedying this deficiency for Pt–Re/Al_2O_3 with a study of the effects on CO adsorption of repeated regeneration cycles in the presence and absence of chlorine during the oxidation step. We hoped to assess not only Pt dispersion but also the surface character of Pt sites in sulphur-free catalysts after the various treatments. Spectroscopic results for monometallic Re/Al_2O_3 and bimetallic Pt-Re/Al_2O_3 which had not been subjected to regeneration procedures are described elsewhere (7, 8), and have established time-dependent behaviour for the interactions between CO and dispersed Re. Bulk metallic phases in the present catalysts have been investigated using XANES (9).

EXPERIMENTAL

Chlorine-free catalyst precursors, designed to contain 0.3 wt% Pt, 0.3 wt% Re, and 0.3 wt% Pt + 0.3 wt% Re after reduction, were prepared by wet impregnation of γ-Al_2O_3 (surface area 110 $m^2\ g^{-1}$) with aqueous solutions of $Pt(NH_3)_4(OH)_2$ and Re_2O_7 (both Johnson Matthey) followed by solvent evaporation and drying in air at 383 K. Two Pt–Re/Al_2O_3 catalysts were prepared, one (Pt–Re(C)) by co-impregnation and one (Pt–Re(S)) by step impregnation involving addition of Pt followed by calcination at 673 K in air before subsequent addition of Re.

Catalyst precursors, either as self-supporting discs for infrared study or as loose powder for H_2 chemisorption measurements, were initially subjected to a treatment (designated *cal*) involving heating (15 K min^{-1}) to 673 K in a flow (60 ml min^{-1}) of dry CO_2-free air, maintaining at 673 K in air for 1 h, evacuating at 673 K (for chemisorption experiments evacuation was replaced by purging with N_2 for 5 min), introducing an H_2 flow (25 ml min^{-1}), raising the temperature to 773 K, and finally reducing at 773 K for 1 h.

In some infrared experiments, spectra of adsorbed CO ($4.5 \times 10^{-4} - 30$ Torr, 295 K) were recorded at every stage of catalyst treatment (4-cm^{-1} resolution using a Perkin–Elmer 1710 FTIR spectrometer). A typical procedure was calcination in air, CO adsorption, reduction, CO adsorption, exposure to air at 295 K for 5 min, CO adsorption, followed by either an oxidation treatment (as for calcination but at

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823 K) or an oxychlorination treatment (as for oxidation but with the air flow also containing 1,2-dichloropropane at 6.0 μl h^{-1} for 0.1 g catalyst). CO adsorption was then monitored again, followed by reduction in H_2 at 773 K for 1 h, CO adsorption, exposure to air at 293 K, and CO adsorption. After the sequence of experiments involving oxidation the Pt–Re catalysts were subjected to a further similar sequence involving oxychlorination.

The initial experiments involved monitoring CO adsorption not only after all the reduction treatments (773 K) but also after calcination (673 K), oxidation (823 K), and oxychlorination (823 K). The adsorption of CO on reduced catalysts alone was then probed for longer series of consecutive treatment cycles. The combination of oxidation/reduction is designated an *oxid* cycle and oxychlorination/reduction is referred to as an *oxy* cycle. Typical total sequences of treatments and monitoring of adsorbed CO after each reduction stage involved the initial *cal* cycle followed by either up to 10 *oxy* cycles or 6 *oxid* cycles followed by up to 3 *oxy* cycles. Catalysts were not cooled to 295 K during the sequences except for prior to CO adsorption and spectroscopic examination.

Similar sequences of *cal* followed by *oxid* and *oxy* cycles involved, after the catalyst reduction stages, measurement of H_2 chemisorption at 298 K by pulsed chemisorption with analysis using a Perkin–Elmer AutoSystem XL gas chromatograph. The amounts of 1,2-dichloropropane in oxychlorination treatments of catalysts used in the chemisorption measurements were 6.0 μl h^{-1} per 100 mg catalyst for the first *oxy* treatment after either a *cal* or an *oxid* cycle and 3.0 μl h^{-1} per 100 mg catalyst for all subsequent *oxy* treatments.

RESULTS

Catalysts after Calcination, Oxidation, or Oxychlorination

Figure 1 shows spectra of CO adsorbed on catalyst precursors which had been subjected to calcination or oxidation treatments. After calcination of Pt/Al_2O_3 precursor an initial band at 2095 cm^{-1} was due to CO adsorbed on an O-covered Pt surface (3, 10). A further band at 2118 cm^{-1} was due to more weakly adsorbed CO on Pt^{4+} sites in the surface of PtO_2 crystallites (3, 11, 12). A weak band at 2172 cm^{-1} is typical of carbonyls of Pt^{2+} (13). A band at 2200 cm^{-1} for high CO pressures, which disappeared on evacuation, was due to CO ligated to Al^{3+}oxid sites in the alumina surface (14).

Apart from the band due to Al^{3+}–CO, spectra of calcined Re/Al_2O_3 precursor showed little evidence for adsorbed CO other than weak bands at 2160 and 2128 cm^{-1} (Fig. 1B) in accordance with conclusions that oxidised Re^{n+} ions do not readily adsorb CO (7, 15). Spectra of CO on calcined (Fig. 1C) or oxidised (Fig. 1D) $Pt–Re/Al_2O_3$ were,

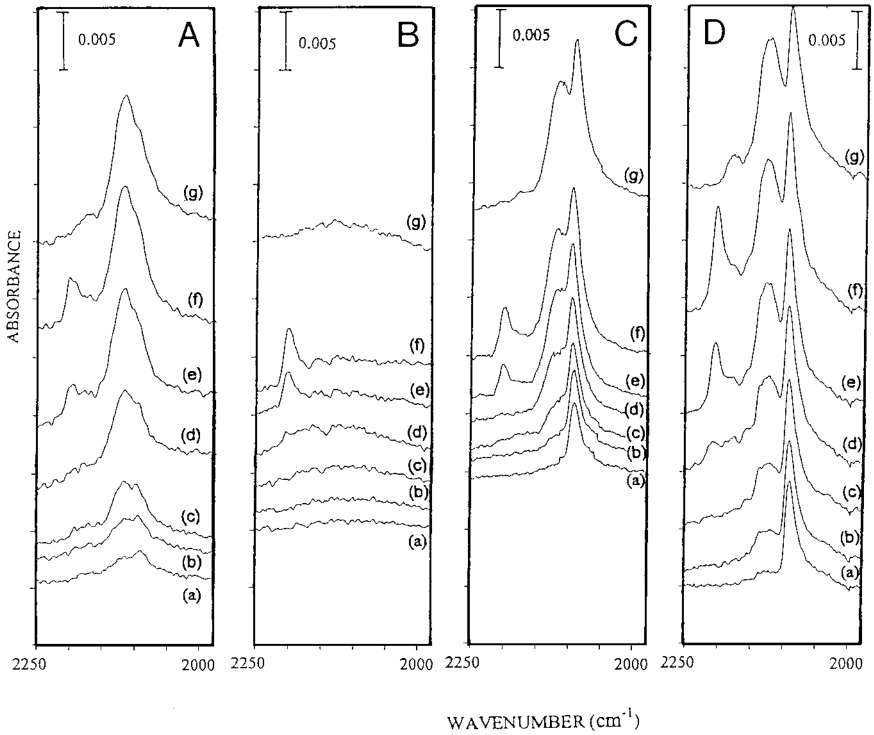

FIG. 1. Spectra of (A) Pt/Al_2O_3 after calcination, (B) Re/Al_2O_3 after calcination, (C) $Pt–Re(C)/Al_2O_3$ after calcination, and (D) $Pt–Re(C)/Al_2O_3$ after oxidation, in contact with CO at pressures of (a) 4.5×10^{-4}, (b) 1.7×10^{-3}, (c) 0.1, (d) 1, (e) 15, and (f) 30 Torr, and (g) subsequent evacuation (30 min, 295 K).

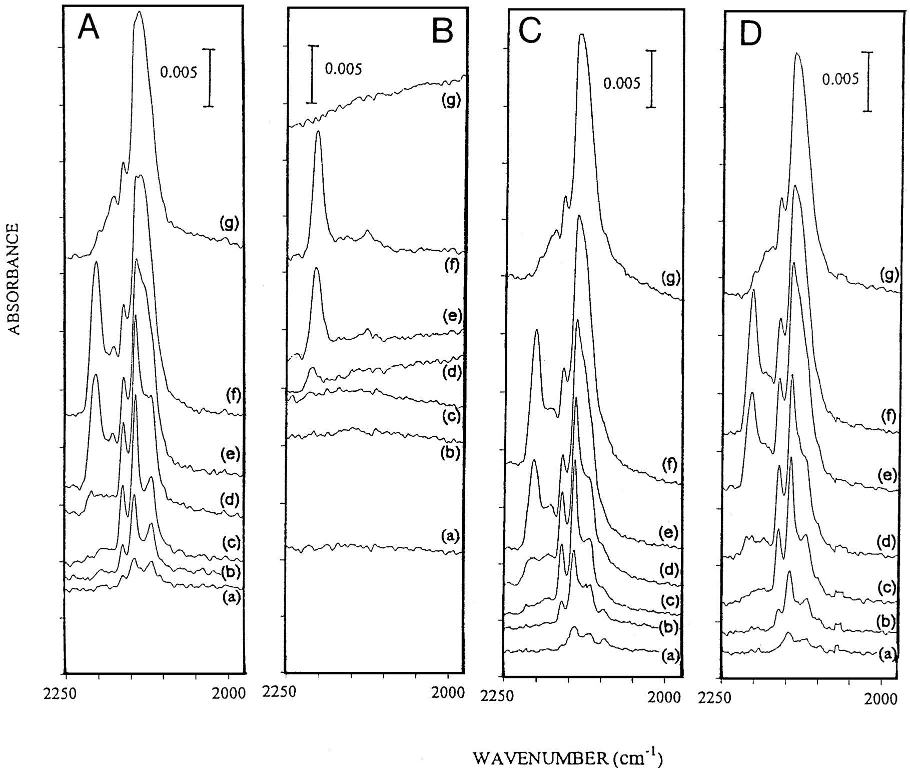

FIG. 2. Spectra after oxychlorination of (A) Pt/Al_2O_3 (first *oxy* after *cal*), (B) Re/Al_2O_3 (first *oxy* after *cal*), (C) Pt–Re(C)/Al_2O_3 (first *oxy* after *cal*), and (D) Pt–Re(C)/Al_2O_3 (first *oxy* after consecutive *cal* and *oxid* cycles), in contact with CO; (a)–(g) are as in Fig. 1.

therefore, dominated by bands at 2118 and 2095 cm^{-1} due to adsorption on PtO_2 and a Pt surface with O-adatoms. The relative intensities of the latter two bands after calcination was the reverse of the result for Pt alone, suggesting that the presence of Re enhanced the partial decomposition of PtO_2 to Pt (12) under oxidising conditions at high temperature.

Spectra of CO adsorbed on oxychlorinated catalysts (Fig. 2) were also dominated by bands due to adsorption at platinum sites. For Re/Al_2O_3 there was only a weak band at 2128 cm^{-1}. For Pt/Al_2O_3 at low CO pressures the band at 2118 cm^{-1} due to adsorption on PtO_2 was accompanied by maxima at 2142 cm^{-1}, ascribed to surface $PtCl_2CO$ (16), and 2162 and 2195 cm^{-1}, attributed to $PtCl_2(CO)_2$ (16–18). The band at 2195 cm^{-1} was distinguished from that at 2200 cm^{-1} by the fact that it did not disappear after evacuation. At higher CO pressures further bands at 2133 (becoming the dominant band) and 2172 cm^{-1} may be ascribed to CO ligated to oxychloro-Pt complexes (2, 19), which promote better spreading of Pt over the alumina surface during oxychlorination (19, 20) than during chlorination in the absence of oxygen when only chloro-Pt complexes are formed (16).

The results for Pt–Re/Al_2O_3 after oxychlorination (Fig. 2) closely resembled those for Pt/Al_2O_3 in terms of both band positions and relative intensities. The presence of Re apparently had little effect on the behaviour of Pt during the oxychlorination process. In accordance with this conclusion XANES studies of the same catalysts showed that oxychlorination resulted in the separation of both components into oxidic species (9).

There were no significant differences between the spectroscopic results for Pt–Re(C)/Al_2O_3, which are figured, and Pt–Re(S)/Al_2O_3.

Hydrogen Chemisorption

The effects on Pt dispersion of catalyst regeneration by oxidation/reduction or oxychlorination/reduction differ (1–3) because of the benefits derived from the spreading of oxychloro-Pt and chloro-Pt complexes over the alumina surface prior to reduction (19, 20). Hydrogen uptakes by Pt/Al_2O_3 after each reduction stage in one series involving a *cal* cycle followed by six *oxy* cycles and a second series involving a *cal* cycle followed by six *oxid* cycles and then two *oxy* cycles (Fig. 3) in general resembled similar results for CO chemisorption on catalysts which had been reduced at 673 K (3) rather than, as here, 773 K. Repeated *oxid* cycles in the absence of chlorine led to progressive Pt sintering, whereas repeated *oxy* cycles maintained or even slightly improved the dispersion. An *oxy* cycle markedly improved the dispersion of sintered Pt but did not give as good a dispersion as was achieved during the series of six *oxy* cycles. The

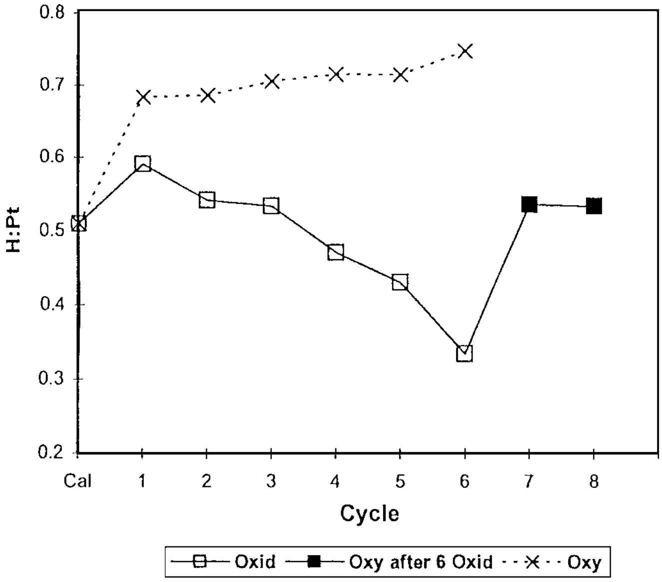

FIG. 3. Dispersion values for Pt/Al_2O_3 after *cal*, *oxid*, and *oxy* cycles.

adverse effects of Pt sintering were only partly countered by one or even two subsequent *oxy* cycles.

The hydrogen chemisorption results for $Pt–Re/Al_2O_3$ (Fig. 4) showed the same general trends as the results for Pt/Al_2O_3, further suggesting that the presence of Re was having little effect on the behaviour of Pt. However, H : Pt values for $Pt–Re/Al_2O_3$ were ca. 27 ± 4% of the values for Pt/Al_2O_3, supporting a previous conclusion that bimetallic particles were formed in the mixed systems (9).

CO Adsorption on Reduced Monometallic Catalysts

The present results for Pt/Al_2O_3 reduced at 773 K resembled spectra of CO on Pt(0.3%)/Al_2O_3 after *cal*, *oxid*, and *oxy* cycles involving reduction at 673 K (3, 21). Detailed results are not, therefore, presented or discussed here as the same interpretations of the results as before are applicable. Briefly, a dominant maximum to the band envelope due to linearly adsorbed CO on Pt was accompanied by a scarcely discernible high-wavenumber shoulder (8) and a low-wavenumber tail possibly containing one (8) or two further bands (21). The dominant maxima for Pt/Al_2O_3 exposed to 15 Torr CO were at 2070, 2068, and 2076 cm^{-1} after *cal*, *oxid*, and *oxy* cycles, respectively. Bands due to bridging CO were difficult to discern after *cal* and *oxid* treatments because the appropriate region of the spectrum was obscured by a broad band at ca. 1830 cm^{-1}, which disappeared after evacuation, due to adsorption on the alumina support (22, 23). This band was observed for CO adsorption on alumina alone. However, there was a clear band at 1848 cm^{-1} for Pt/Al_2O_3 after *oxy* cycles. The areas under the band envelope due to Pt–CO decreased with increasing number of consecutive *oxid* cycles in accordance with the losses in dispersion identified by H_2 chemisorption. In contrast, the band area was roughly constant after consecutive *oxy* cycles.

Spectra of CO on supported Re vary with time, and, therefore, spectra were recorded for various times up to 1 h before evacuation and further treatment. Figure 5 shows representative comparisons of the spectra after specific cycles in overall sequences of seven cycles involving *cal*, *oxid* 1

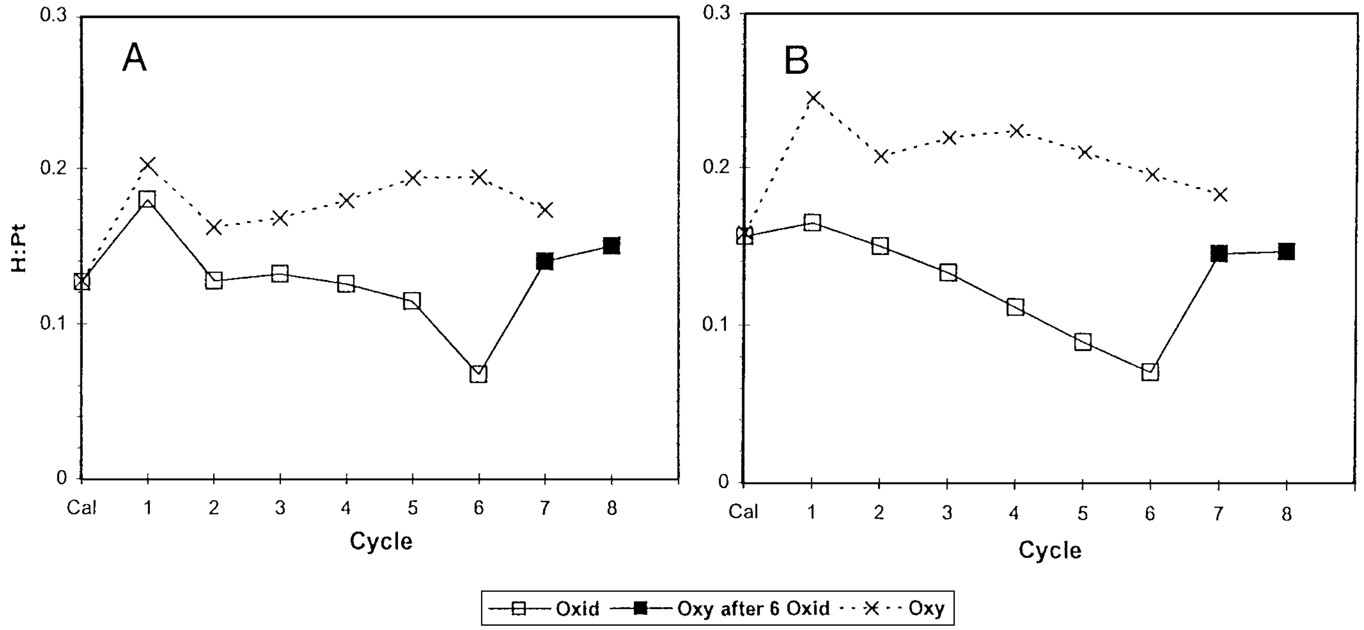

FIG. 4. Dispersion values for (A) Pt–Re(C)/Al_2O_3 and (B) Pt–Re(S)/Al_2O_3 after *cal*, *oxid*, and *oxy* cycles.

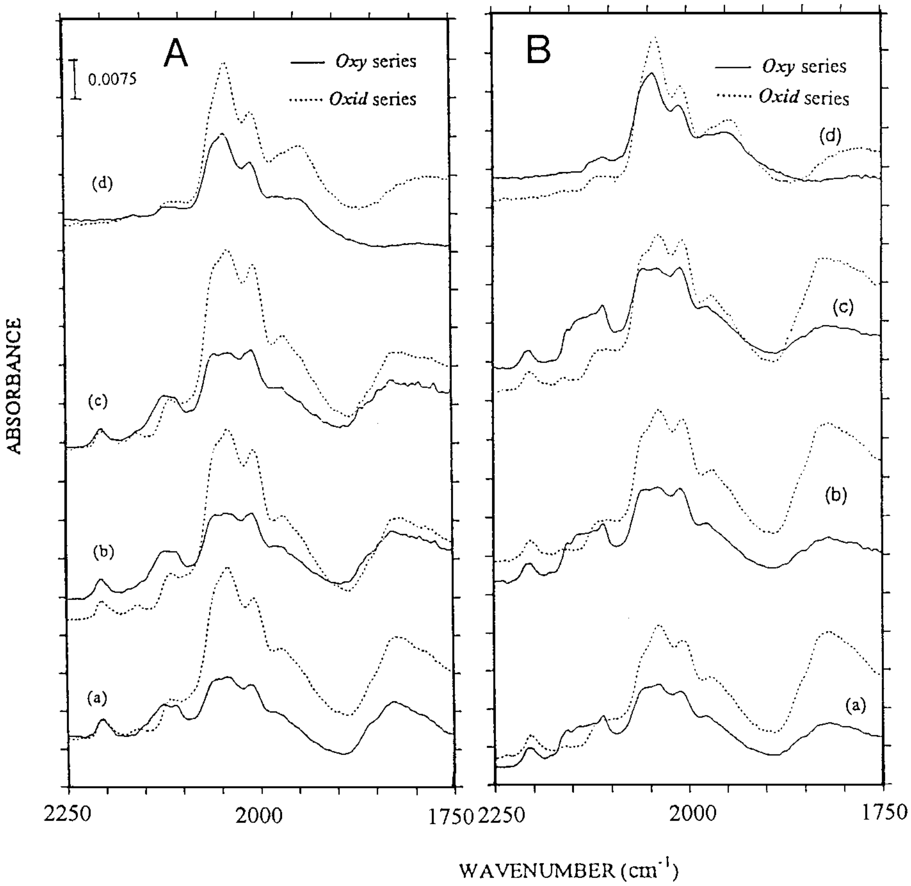

FIG. 5. Comparative spectra of Re/Al_2O_3 after (A) *oxid* 1 and *oxy* 1 cycles, and (B) *oxid* 6 and *oxy* 6 cycles, and exposure to CO (15 Torr) for (a) 5 min, (b) 1/2 h, (c) 1 h, followed by (d) evacuation (1/2 h).

to *oxid* 6, and *cal, oxy* 1 to *oxy* 6. Band assignments are based on deconvoluted spectra for catalysts with a higher Re loading (1 wt%) which were left for up to 12 h in contact with CO (8). A band at 2040 cm^{-1} is ascribed to CO linearly adsorbed at Re^0 sites (7). Bands at 2112, 2060, 2006, and 1972 cm^{-1} grew in intensity with time and are attributed to $Re_2(CO)_{10}$ (7, 24, 25). Further bands at 2030 and 1937 cm^{-1} due to $Re(CO)_3$ (7, 24, 25) also grew with time and were particularly noticeable after the removal of CO by evacuation. A weak band at 2154 cm^{-1} was probably due to $Re(CO)_5$ (24, 25). As before (7, 8) the results were consistent with a slow reaction sequence Re–CO $\rightarrow$ $Re_2(CO)_{10}$ $\rightarrow$ $Re(CO)_3$ with a small amount of $Re(CO)_5$ appearing in parallel to the $Re_2(CO)_{10}$. The bands at 2200 and 1830 cm^{-1} in Fig. 5 were due to CO adsorption on alumina.

Repeated *oxid* cycles reduced the intensity of the overall band envelope due to Re complexes although after evacuation, which led to spectra containing prominent bands at 2030 and 1937 cm^{-1} due to $Re(CO)_3$, the intensities and shapes of the band envelopes were unchanged as a function of increasing number of *oxid* cycles. It therefore appears that smaller amounts of Re–CO and $Re_2(CO)_{10}$ were formed after several *oxid* cycles than after the first *oxid* cycle, but that the amounts of $Re(CO)_3$ formed remained the same. All the bands present during the sequence of *oxid* cycles were also present during the series of *oxy* cycles with the possible exception of the weak band at 2154 cm^{-1} due to $Re(CO)_5$. However, all the bands were much weaker after *oxy* cycles, this difference becoming less marked with increasing cycle number. The presence of chlorine decreased the availability of Re for interaction and reaction with CO but, in contrast to the result for Cl-free catalysts, the opportunity for reaction was not decreased with further treatment cycles. The presence of chlorine shifted most of the bands by ca. 5 ± 2 cm^{-1} towards higher wavenumbers and also slightly changed the ratio of Re–CO to $Re_2(CO)_{10}$ formed in favour of the latter. A group of additional bands, not present for Cl-free catalysts, appeared as a broad envelope with maxima apparent at 2155, 2140, 2125, and 2109 cm^{-1} after the sixth *oxy* cycle (Fig. 5B). However, this group of bands only appeared after several (>4) *oxy* cycles, and not for the first few *oxy* cycles after either a *cal* or several *oxid* cycles, showing that their appearance resulted from a cumulative effect of a series of oxychlorination treatments.

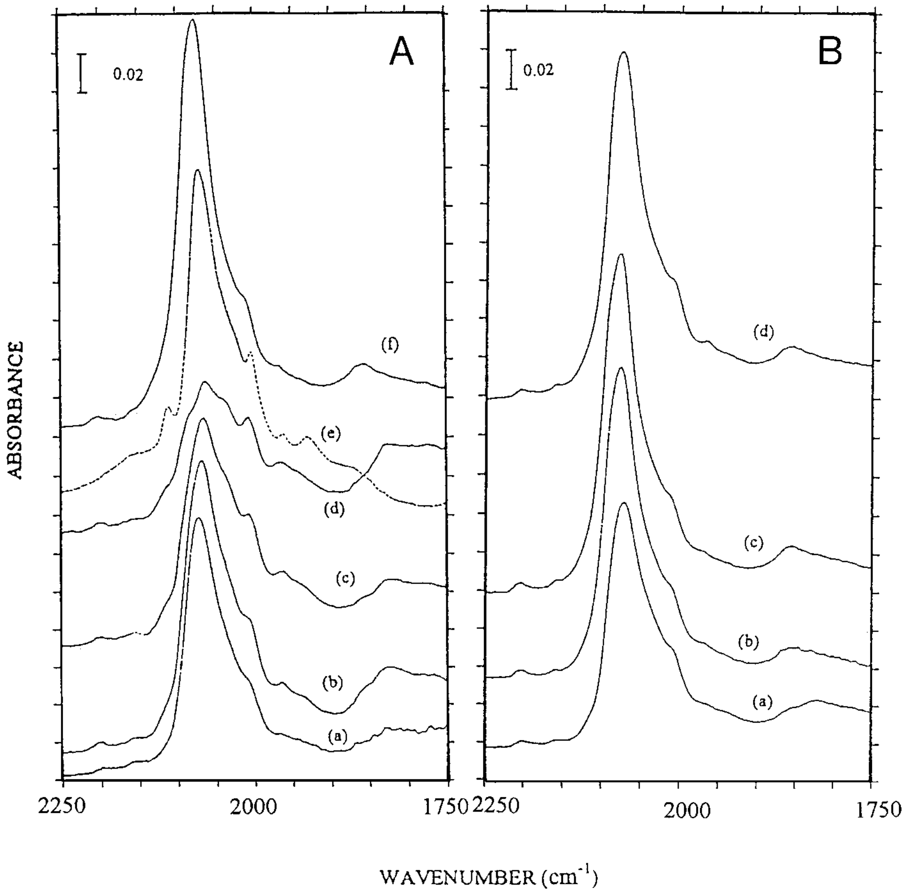

FIG. 6. Spectra of Pt–Re(S)/Al_2O_3 exposed to CO (15 Torr) for 1/2 h after the treatment cycles (A), (a) *cal*, (b) *oxid* 1, (c) *oxid* 3, (d) *oxid* 6, (e) *oxy* 1, (f) *oxy* 3, and (B), (a) *cal*, (b) *oxy* 1, (c) *oxy* 3, (d) *oxy* 6.

The bands, which are attributed to ligation of CO to surface chloro-Re species, disappeared on evacuation, leaving spectra closely similar to those after early *oxy* cycles.

CO Adsorption on Reduced Bimetallic Catalysts

Spectra of Pt–Re/Al_2O_3 were dominated by the band envelope with a maximum at 2075 cm^{-1} due to linear CO on Pt sites (Fig. 6). After a *cal* or an initial *oxid* cycle only shoulders at 2115, 2006, and 1962 cm^{-1} due to $Re_2(CO)_{10}$ and 1937 cm^{-1} due to $Re(CO)_3$, and a weak band at 2154 cm^{-1} due to $Re(CO)_5$, provided evidence for the presence of exposed Re. However, increasing number of *oxid* cycles led to the progressive loss of Pt adsorption sites and the appearance of more prominent, but no more intense, bands due to Re complexes (Fig. 6A(d)). Comparisons of band intensities for Re alone and Pt–Re were hampered by the overlap with bands due to adsorption on Pt, but they indicated that, as before (8), the amount of exposed Re was considerably enhanced in Pt–Re/Al_2O_3 compared with Re/Al_2O_3. A pronounced shoulder at 2085 cm^{-1} after six *oxid* cycles was not present in spectra of Re/Al_2O_3 but was probably (8) contained in the band envelope for CO on Pt in Pt–Re/Al_2O_3 after the first and all subsequent *oxid* cycles. Thus, although a high proportion of Pt sites disappeared as a result of oxidative sintering, high-coordination Pt sites in extended arrays of Pt atoms (3, 10, 12) were retained. Increasing particle size resulting from sintering might in any case be expected to enlarge exposed Pt arrays, although the result also supports a previous contention (8) that terraces of Pt atoms were not decorated by Re.

An *oxy* cycle after six *oxid* cycles restored the strong maximum at 2075 cm^{-1} due to Pt–CO whilst retaining bands at 2112, 2006, and 1963 cm^{-1} characteristic of $Re_2(CO)_{10}$, and at 1930 cm^{-1} due to $Re(CO)_3$. A second *oxy* cycle gave a further considerable enhancement in the intensity of the band due to Pt–CO which was shifted to 2078 cm^{-1}, and also gave a band at 1856 cm^{-1} due to bridged CO on Pt. However, bands due to Re-carbonyls were less well resolved, partly because they were more heavily obscured by the Pt–CO band, and partly because they were apparently reduced in intensity. Spectra of Pt–Re/Al_2O_3 exposed to CO after a first *oxy* cycle following a *cal* cycle or after further *oxy* cycles resembled the result for a second *oxy* cycle following

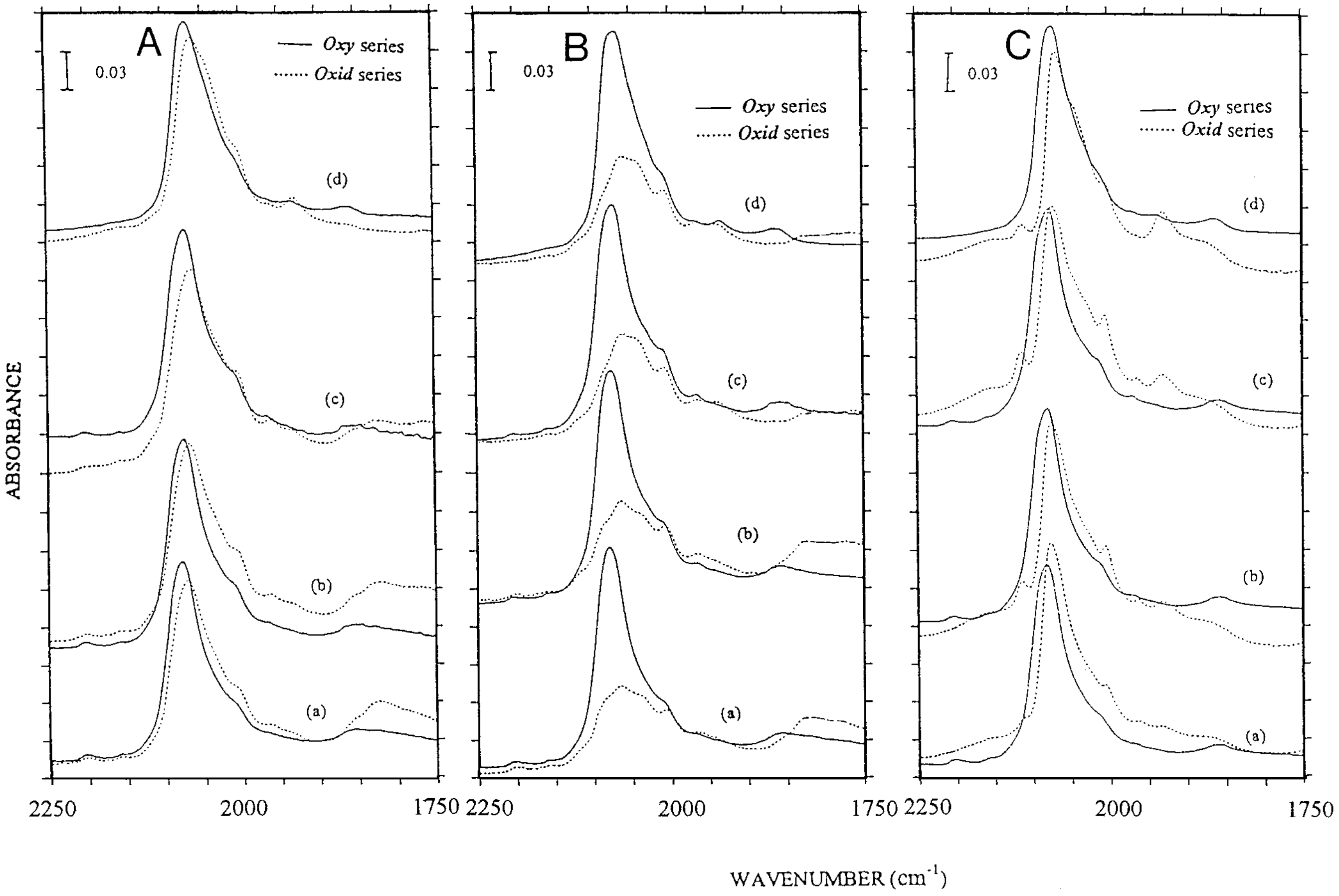

FIG. 7. Comparative spectra of Pt–Re(S)/Al$_2$O$_3$ after (A) *oxid* 1 and *oxy* 1 cycles, (B) *oxid* 6 and *oxy* 6 cycles, and (C) *oxy* 1 after 6 *oxid* cycles and *oxy* 7, and exposure to CO (15 Torr) for (a) 5 min, (b) 1/2 h, (c) 1 h, and (d) followed by evacuation (1/2 h).

six *oxid* cycles (Fig. 6B). Six *oxid* cycles generated a catalyst structure which required more than one *oxy* cycle to generate the typical result after all other *oxy* cycles, although this effect was much more marked for Pt–Re(S)/Al$_2$O$_3$ than for Pt–Re(C)/Al$_2$O$_3$.

The spectra in Fig. 7 emphasise the effects of chlorine on catalyst character. Only small differences in CO adsorption behaviour existed after the first *oxid* and *oxy* cycles following a *cal* cycle, although the presence of chlorine slightly shifted the bands towards higher wavenumbers for both Pt–CO and Re-carbonyl species (Fig. 7A). However, the marked decrease in Pt surface induced by several consecutive *oxid* treatments was in contrast to the stabilising effect of chlorine on the Pt surface during repeated *oxy* treatments (Fig. 7B), which also favoured bridging sites for CO adsorption (1856 cm^{-1}). The intensities of bands assigned to Re-carbonyl species were relatively unaffected by the presence or absence of chlorine. Comparison of spectra following an *oxy* cycle after either six *oxid* treatments or six *oxy* treatments shows that both Re$_2$(CO)$_{10}$ and Re(CO)$_3$ were more favoured after the series of Cl-free pretreatments although the amounts of Pt–CO generated were about the same (Fig. 7C).

Areas under the infrared band envelopes after individual steps in the sequences of *oxid* and *oxy* treatments have been determined and, despite limitations posed by different extinction coefficients for different bands, may be used to gain an approximate measure of the effects of the treatments on metal dispersion. Despite the significant decrease in the H$_2$ uptakes for Pt–Re/Al$_2$O$_3$ compared with Pt/Al$_2$O$_3$ after a *cal* cycle, the infrared band intensities for adsorbed CO were slightly higher for Pt–Re than for Pt alone. After subtraction from the intensities for Pt–Re of estimates of the small contributions from the bands due to Re–CO species, the band intensities for Pt–CO were, as before (8), similar to those for Pt alone. Thus H$_2$ and CO adsorption apparently gave conflicting information about the influence of Re on Pt dispersion.The results shown in Fig. 8 have been normalised for each individual pressed disc by dividing the values by the value after the initial *cal* cycle. Oxidation of Re/Al$_2$O$_3$ at 823 K (*oxid*) rather than 673 K (*cal*) favoured improved Re availability for the adsorption of CO or reaction with

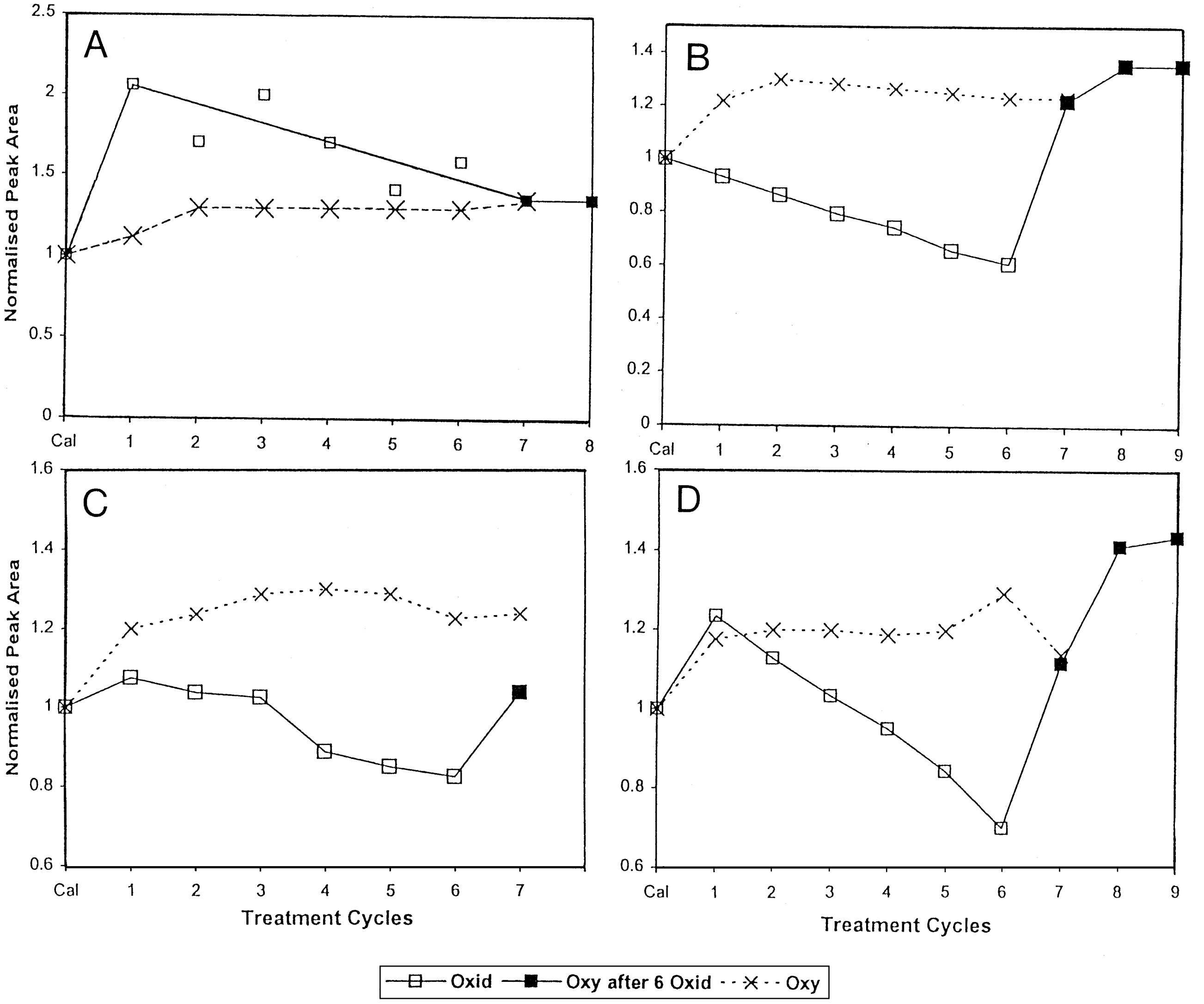

FIG. 8. Normalised ν_{CO} band areas after 1/2 h contact between CO (15 Torr) and (A) Re/Al_2O_3, (B) Pt/Al_2O_3, (C) Pt–Re $(C)/Al_2O_3$, and (D) Pt–Re$(S)/Al_2O_3$.

CO, although the effect was reduced by repeated *oxid* cycles or by the addition of chlorine. In contrast for Pt/Al_2O_3, as before (1–3), chlorine favoured enhanced Pt dispersion whereas repeated *oxid* cycles led to Pt sintering, redispersion being achieved by subsequent oxychlorination and reduction. The results for Pt–Re catalysts reflected the results for Pt alone and were consistent with the H_2 chemisorption data (Fig. 4). The trends were dominated by effects involving Pt rather than Re, clearly demonstrating the efficacy of oxychlorination of Pt–Re/Al_2O_3 catalysts for maintaining and restoring Pt surface area.

DISCUSSION

The infrared results for calcined, oxidised, and oxychlorinated catalysts support conclusions that the Re and Pt components were segregated after oxidative treatments (9, 26, 27). XANES showed that after calcination the Pt was in small particles with local order similar to that for PtO_2 (9), this being consistent with the appearance of an infrared band typical of CO adsorbed on PtO_2 for calcined and oxidised Pt–Re/Al_2O_3 (Fig. 6). However, the infrared spectra also show that oxidation of Pt–Re/Al_2O_3 in air at 673 or 823 K led to partial decomposition of PtO_2 to give Pt^0 particles with a surface layer of O-adatoms. Yao *et al.* (28) reported that PtO_2 decomposes to Pt^0 at 823 K, and XRD results for a Pt–Sn/Al_2O_3 catalyst confirm the formation of Pt^0 particles together with PtO_2 in air at 823 K (12).

The lack of adsorption of CO at Re^{n+} sites (7, 15) precluded the infrared spectra giving useful information about the state of Re in oxidised or oxychlorinated Pt–Re/Al_2O_3, although XANES has shown that oxidic Re^{7+} species were probably dominant (9), and, contrary to some suggestions (27, 29), that Re oxychloride is not formed. The close similarity between the spectra of oxychlorinated Pt/Al_2O_3 and Pt–Re/Al_2O_3 exposed to CO (Fig. 2) establishes that the formation of chloro-Pt and oxychloro-Pt complexes were unaffected by the presence of Re. A previous conclusion in accordance with this result was that Re is not involved in Pt redispersion (30). Here, oxychlorination as a means of redispersing Pt by the spreading of chloro-Pt and particularly oxychloro-Pt complexes over alumina (2, 19, 20) was equally effective in the absence or presence of Re. The presence of chlorine favoured the Cl-containing complexes at the expense of Pt^0 and PtO_2, which were dominant after Cl-free oxidation. Malet *et al.* (29) concluded that the presence of chlorine in Pt–Re/Al_2O_3 influenced the mobility of metal precursors and hence the metallic structure of reduced catalyst. The results for Pt–Re/Al_2O_3 contrast with those for Pt–Sn/Al_2O_3, for which, although chloro-Pt and oxychloro-Pt complexes were formed, Pt^0 remained a significant catalyst component even after oxychlorination (3, 12).

A report that the addition of Re to Pt/Al_2O_3 greatly increases H_2 uptake (31) is not consistent with the present ca. 73% decrease in H_2 adsorption for Pt–Re/Al_2O_3 compared with Pt/Al_2O_3. The Re component of the mixed catalysts does not chemisorb H_2 (32, 33), and therefore the H_2 uptakes only reflect the adsorption behaviour of Pt. The conclusion from the infrared spectra that more Re^0 was exposed in Pt–Re/Al_2O_3 than in Re/Al_2O_3 might be explicable by enhanced reduction of Re^{n+} species catalysed by Pt (31), but it is also consistent with proposals that either Re enrichment occurred in exposed surfaces (9) or all the Re atoms present were in the surface of Re particles or alloy particles with Pt (34). However, the apparently logical corollary that the reduced H_2 uptake on adding Re reflected simply a loss in the number of exposed Pt atoms due to decoration of the surfaces of Pt or alloy particles by Re is not compatible with the similar CO uptakes derived from infrared band intensities for Pt–Re/Al_2O_3 and Pt/Al_2O_3. Previously, marked reductions in H_2 chemisorption on adding Re to Pt/Al_2O_3 have been attributed to Pt–Re alloy formation (35–37). Similar results for Sn/Pt(111) surface alloys were shown by parallel measurements of the adsorption of gas-phase H-atoms to be due to a substantial increase in the activation energy for the dissociative adsorption of H_2 and not a reduction in the availability of surface Pt atoms (38). The descrepancy between the H_2 and CO uptakes for Pt–Re/Al_2O_3 may be similarly explained, and therefore may indicate, in accordance with XANES results (9), that the Pt component was predominantly alloyed with Re in bimetallic particles.

The extent of Pt–Re interaction in Pt–Re/Al_2O_3 catalysts depends not only on the extent of catalyst hydration prior to reduction (37) but also on the effects of chlorine both prior to and during reduction (9, 27, 36, 39–41). Catalyst dehydration decreases the extent of Pt–Re interaction (37), but this can be countered by the addition of chlorine, which has been reported to enhance bimetallic cluster formation by increasing the mobility of Re in the system (27). Conflicting evidence suggested that metal oxychloro complexes were strongly bonded to the alumina surface; their mobility was therefore inhibited, and hence they gave catalysts with lower alloy content than that for Cl-free catalysts (29, 39). Prestvik *et al.* (36) concluded that loss of chlorine leads to increased Re oxide mobility and hence more alloy formation. A decrease in alloy formation induced by chlorine was attributed by Munuera *et al.* (41) to reduced mobility of Re^{4+} species strongly interacting with alumina. For the present catalysts the discrepancy between the effects of added Re on CO and H_2 adsorption were equally apparent for Cl-free and Cl-containing catalysts showing, in accordance with XANES results (9), that alloy was the dominant metallic component in the presence or absence of chlorine.

For Pt–Re/Al_2O_3, no matter whether it was judged by the H_2 adsorption results (Fig. 4) or the ν_{CO} infrared band intensities (Fig. 8), the presence of chlorine induced, as before (29, 39, 40), higher metal dispersions. Despite the parallel with results for Pt alone (Figs. 3 and 8), it may be too simplistic to argue (29, 36, 39, 41) that chlorine inhibits the mobilities of Re precursors and therefore favours an increased proportion of segregated Pt^0 particles in reduced Cl-containing catalysts. XANES has shown that Re reduction was easier after the addition of chlorine (9). Chlorine favours the spreading of chloro-Pt and oxychloro-Pt complexes over alumina (20, 21), and this leads to better Pt dispersions in the presence of chlorine (2). As the Pt/Al_2O_3 and Pt–Re/Al_2O_3 catalysts generated similar precursor states of Pt during oxychlorination (Fig. 2), the better dispersions for Pt–Re/Al_2O_3 after *oxy* cycles rather than *oxid* cycles could simply reflect the improved dispersion of Pt and no change in the ease of incorporation of Re into alloy particles with Pt. Chlorine would then assist the formation of more smaller particles with the same surface and bulk structures as those generated after *oxid* cycles. The increase in Pt dispersion could be explained, therefore, not only in terms of decreases in the mobility of oxidised Re species and an increase in the amount of segregated Pt (29, 36, 39, 40) but also in terms of the enhanced mobility of Pt-complexes involving chlorine leading to enhanced dispersion of alloy particles. The present catalysts did not contain chloro-Re or oxychloro-Re complexes after oxychlorination (9). Indirect evidence here for Re–Cl species only appeared for Re/Al_2O_3 after several *oxy* cycles (Fig. 5B) and was absent for Pt–Re/Al_2O_3. However, XANES evidence for Re–Cl interactions appeared during the reduction stage of catalyst preparation, suggesting that the presence of chlorine influenced the mechanism of incorporation of Re into alloy particles (9). The formation of bimetallic particles with a monometallic Pt core and a Re-rich surface (9) would perhaps support the suggestion that the Cl-induced improved dispersion of Pt followed by incorporation of Re into the particle surfaces accounts for the enhanced uptakes of H_2 and CO for *oxy* rather than *oxid* cycles. The enrichment of exposed Re in Pt–Re/Al_2O_3, shown by comparison of the infrared band intensities for CO interacting with Re in Re/Al_2O_3 and Pt–Re/Al_2O_3, is also consistent with the spreading of Re over Pt particles rather than the presence of segregated Re particles.

For Pt/Al_2O_3 after six *oxid* cycles the uptakes of H_2 and CO were 66 and 62%, respectively, of their values after the first *cal* cycle. The sintering effect of repeated *oxid* cycles was similarly reflected by the H_2 and CO uptakes. However, for Pt–Re(C)/Al_2O_3 and Pt–Re(S)/Al_2O_3 the corresponding percentages were 55 and 82%, and 43 and 72%, respectively. Thus the H_2 uptakes were proportionally reduced much more than the CO uptakes, suggesting that surface alloying was enhanced by repeated *oxid* treatments. Sintering not only reduced the number of exposed Pt atoms (CO adsorption) but also increased the proportion of exposed Pt atoms which, due to the influence of Re, were unable to dissociatively adsorb H_2. In contrast, the proportion of the Pt surface which could not dissociate H_2 was apparently unaffected by repeated *oxy* cycles, which also had little effect on XANES results or activities and selectivities for heptane reforming (9). Thus oxychlorination not only maintained Pt surface area but also inhibited the additional spreading of Re over the Pt surfaces.

Bond and Cunningham (42) proposed from catalytic studies involving Pt–Re/Al_2O_3 containing chlorine that Re preferentially occupied high-coordination Pt atom sites in low-index planes. This provides one plausible explanation for the combined H_2 chemisorption uptakes here and XANES results for the same catalysts (9). However, the nearly identical ν_{CO} infrared band intensities for Pt/Al_2O_3 and Pt–Re/Al_2O_3 after the initial *cal* cycles are only explicable if the numbers of exposed Pt atoms in short terrace sites were similar in the monometallic and bimetallic catalysts, and this could only be achieved with a greater number of smaller particles in Pt–Re/Al_2O_3 than in Pt/Al_2O_3. In accordance with this conclusion, Bond and Cunningham (42) reconciled their results with apparently conflicting data (43) by proposing that catalysis mainly occurred on very small highly dispersed particles. The retention of at least some terrace sites is consistent with the drop in H_2 adsorption to ca. 27% of its value for Pt/Al_2O_3, a much smaller decrease than might be expected for more efficient complete alloying of Pt sites in low-index planes (38). Re, therefore, maintains the total area of exposed Pt but reduces particle and terrace sizes, providing a higher proportion of Pt atoms which were unable to dissociate H_2 because of the influence of Re at adjacent sites. A corollary is that the mechanism of particle formation (27) must depend not only on the ease of separate (9) dispersion of Pt in a precursor state during oxidation or oxychlorination before reduction but also on the extent of dispersion of Re-species before reduction and/or the incorporation of Re into bimetallic particles during reduction. Cl favours the improved dispersion of Pt precursor complexes during oxychlorination and also probably (9) facilitates the formation of small bimetallic particles during reduction. An analogy exists with Pt–Sn/Al_2O_3 catalysts (12) for which oxychlorination generated segregated Sn and Pt precursors, but reduction gave Pt–Sn alloy particles which were not formed in the absence of Cl.

The present conclusions relate to an earlier discussion (8) of infrared spectra of CO adsorbed on Pt–Re/Al_2O_3 for which H_2 chemisorption and XANES results were not available, and for which it was concluded that short terraces on Pt or Pt–Re particles did not contain Re atoms which were located at kink or edge sites or spread over the alumina surface. The previous catalysts were subjected to pretreatments and reduction at different temperatures from those adopted here but gave results which were completely consistent with the present spectra. Direct information on the occupancy of kink, step, or edge sites by Re was precluded by the relevant region of the spectrum for CO on these sites (3, 22) being obscured by bands due to CO interacting with Re. The previous (8) and present conclusions would, however, be compatible with a model in which very small bimetallic particles (42) have a concentration of Re atoms at edge and apex sites which surround small Pt^0 terraces. This suggestion differs from that of Bond and Cunningham (42), although they commented that small ensembles of Pt atoms influenced by neighbouring Re atoms may still be present. The catalytic results were better rationalised in terms of Re at sites in low-index planes (42). Of course, if the siting of the exposed Re atoms was nonselective then a proportion of both plane ensemble and edge Pt sites would be available for adsorption and catalysis.

CONCLUSIONS

(a) Oxychlorination of Pt–Re/Al_2O_3 catalyst generated chloro-Pt and oxychloro-Pt complexes independently of the presence of Re, and promoted enhanced spreading of Pt species over the alumina support, thus leading to an improved Pt dispersion after subsequent reduction.

(b) The dispersions of Pt in Pt/Al_2O_3 and Pt–Re/Al_2O_3 were similar, but H_2 chemisorption was considerably reduced by the addition of Re. The Pt–Re catalyst contained very small bimetallic particles with Re surface enrichment. Small ensembles of-high coordination Pt atoms were present, although Re atoms may have been located at both edge and ensemble sites.

(c) The subjection of Pt–Re/Al_2O_3 to repeated oxidation/reduction cycles led to sintering and enhanced coverage of bimetallic particles by Re. These effects were reversed by oxychlorination followed by reduction.

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