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Infrared Studies of Pt and Pt–Re Reforming Catalysts

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Infrared studies of adsorbed CO and NO on Pt/Al_2O_3, Re/Al_2O_3, and $Pt–Re/Al_2O_3$ were made to obtain information on the surface properties of typical Pt and Pt–Re reforming catalysts. Both fresh catalysts and used catalysts which had been regenerated many times in refinery units were studied. Pt and Re concentrations ranged from 0.3 to 1.2 wt%. After suitable pretreatment, the areas and chemical nature of exposed Pt and Re could be estimated from the intensities and frequencies of infrared bands from adsorbed NO or CO. Various pretreatments were studied to determine the conditions most likely to cause rapid loss of metal surface area. Rejuvenation of badly deteriorated catalysts by treatment with Cl_2 or $CCl_4 + O_2$ was also investigated. No evidence was found for the formation of Pt–Re "alloys." Pt and Re appeared to behave independently on the surface. Surface areas of both metals were lost much more rapidly during heating in O_2 (or in a preoxidized state) than on heating in H_2. Both could be restored by rejuvenation with Cl_2 or $CCl_4 + O_2$. Loss of Re area, normally much less rapid than loss of Pt area, is inconsequential under conditions where Pt area is preserved.

INTRODUCTION

Platinum reforming catalysts normally contain less than 1% Pt by weight, dispersed on a high-area alumina support. Economic incentives for using this platinum as efficiently as possible, and for extending catalyst life, are great. The nature of the supported platinum and the possible role of interactions with the support in its catalytic behavior are also subjects of considerable scientific interest. Much excellent research on platinum reforming catalysts was carried out in the 1950s, and work has continued in this area to the present (*1–10*). Additional impetus has been given such research in recent years by the development and commercial use of reforming catalysts containing rhenium plus platinum which deactivate more slowly than conventional Pt reforming catalysts (*11, 12*). The exact role of rhenium in improving the performance of reforming catalysts is not yet clear, and possible interactions of Re with Pt to form "alloys" or bimetallic clusters also remain conjectural.

It has been previously shown that Pt can exist on alumina supports in a very high degree of dispersion (*1–4*) and that redispersion of Pt, which has grown fairly large crystals, is possible to at least some extent (*5–8*). Considerable confusion exists, however, concerning the extent to which redispersion can be achieved and the conditions under which it occurs when Pt/Al_2O_3 catalysts are heated in O_2 (*8, 9*). Under most conditions, any improvement in dispersion with O_2 alone appears small, and Pt area losses appear to be more normal at higher temperatures (*10*). In practice, it is known that a very high degree of Pt

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redispersion can be achieved by treatment of used catalysts with combinations of Cl_2, air, and H_2O or with organic chlorides preheated in air (*5, 6*). Very little has appeared on these subjects in the scientific literature, however, and what has been published often appears confusing and inconclusive.

Published studies on rhenium/alumina catalysts are more recent (*13–18*). Much uncertainty exists as to the extent to which reduction of the rhenium occurs under normal process conditions (*13–15, 17*). Rhenium has been found to be redispersed on alumina under oxidizing conditions (*17*).

Chemisorption methods have been used for many years to evaluate dispersion of metals and have been applied to determine separately dispersion of Pt and Re in Pt–Re catalysts (*18*). These methods can give ambiguous results, however, because chemisorption may be occurring in ways other than those assumed to be responsible for the adsorption or, in some cases (e.g., H_2), chemisorption may not occur on well dispersed Re (*17*).

Infrared spectroscopy has been used for over 20 years to study supported metals through the use of adsorbed probe molecules such as CO or NO (*19, 20*). Such studies on Pt/Al_2O_3 (*21–23*) or Re/Al_2O_3 (*16*) have usually been made on catalysts containing 5 to 25% metal and on alumina supports not normally used for reforming catalysts. Infrared study has also been made of 10% Re/SiO_2 (*24*). This showed the Re to be well reduced after reduction in flowing H_2 at 500°C.

The apparent total absence of published infrared studies of Pt–Re catalysts typical of those used commercially is somewhat surprising considering the additional information which infrared can provide, not only on the degree of dispersion of the individual metals, but also on their chemical nature and possible interactions with the support and with one another. While infrared study is relatively time consuming and will probably not replace conventional chemisorption and X-ray methods for routine evaluation of metals dispersion, it can be invaluable in shedding further light on what is actually occurring on a catalyst surface during and following various pretreatments or in the course of catalyst deactivation and in verifying the assumptions made in conventional studies.

METHODS

Thin catalyst wafers were used for infrared study. These were typically made by pressing 0.25 or 0.30 g of powdered catalyst in a 1.25-in.-i.d. cylindrical steel die, without use of a binder, at roughly 5 tons/in.^{2} A suitable infrared cell permitted pretreatment of these wafers *in vacuo* or in a controlled atmosphere at temperatures up to 900°C (*25*). The procedures used for sample pretreatment were also generally as previously described (*25*). Spectra of adsorbed CO or NO were then recorded at 5–7 Torr of pressure. For treatments outside the ir cell, the catalyst wafers were placed in a 1 × 14-in. Vycor tube and heated in flowing gas (at 1 atm of pressure). For wet Cl_2 + air rejuvenation, water-saturated Cl_2 (40 ml/min) and air (50 ml/min) streams were combined, giving a 90 ml/min flow. Catalysts were typically heated 1 to 4 hr at 500°C. Rejuvenation of catalysts with $CCl_4 + O_2$ was also studied briefly. A catalyst which had shown a major loss of Pt area was heated for 64 hr in the infrared cell at 500°C in 200 Torr of O_2 + 10 Torr of CCl_4.

The catalyst studied were either commercial Pt or Pt–Re catalysts, made by impregnation of pure γ-alumina (initial surface area approximately 250 m^2/g) with chloroplatinic acid and/or perrhenic acid, or were experimental catalysts of similar composition and preparation made in this laboratory. In the instances where

TABLE 1

Data on Fresh and Used Pt/Al_2O_3 Catalysts[a]

Catalyst	Number of regenerations	Pt (%)	Surface area (m^2/g)	Pt growth[b]		Fe (%)
				(%)	(Å)	
X (fresh)	0	0.8	194	0	—	0
Y (fresh)	0	0.6	218	0	—	0
A	249	0.8	105	48	300	0.39
B	541	0.6	116	30	200	1.00
C	310	0.8	118	60	158	0.62
D	224	0.6	124	—	—	2.26
E	525	0.6	85	50	120	3.00
F	541	0.4	117	5	Slight growth	0.97

[a] All used, catalysts had been rejuvenated in wet Cl_2 + air with subsequent steam treatment to reduce the chloride level to 0.7 wt% before initial infrared study.

[b] By X-ray study of the catalyst before rejuvenation; no crystallinity could be observed after rejuvenation.

used commercial catalyst samples were studied the samples had been taken from commercial reforming reactors. Properties of the Pt catalysts studied are shown in Table 1. The fresh Pt–Re catalysts were similar to fresh Pt catalysts except that they contained Re in addition to Pt. Chloride levels varied but normally ranged from 0.3 to 0.8 wt%. They were higher on some rejuvenated catalysts.

RESULTS AND DISCUSSION

The general spectral features of Pt/Al_2O_3 and Pt–Re/Al_2O_3 catalysts were those of the alumina support similarly pretreated.

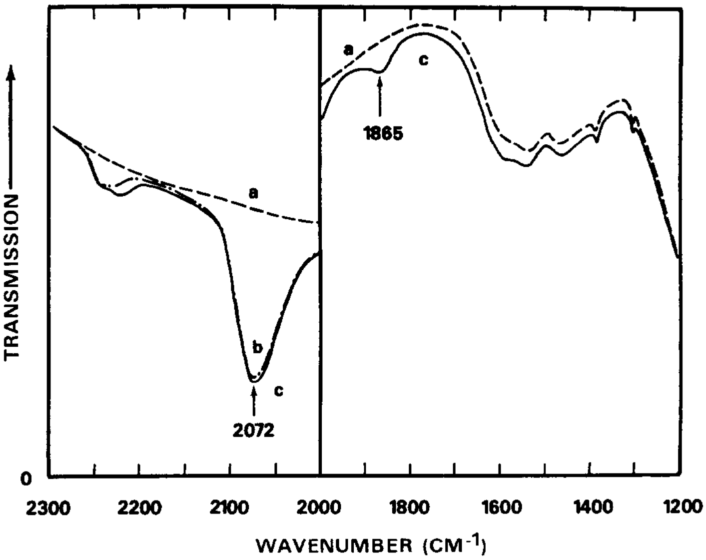

FIG. 1. Spectra of CO adsorbed on 0.6% Pt/Al_2O_3(Y): (a) after evacuation at 600°C; (b) *a* + 1.3 Torr of CO; (c) *a* + 7.0 Torr of CO.

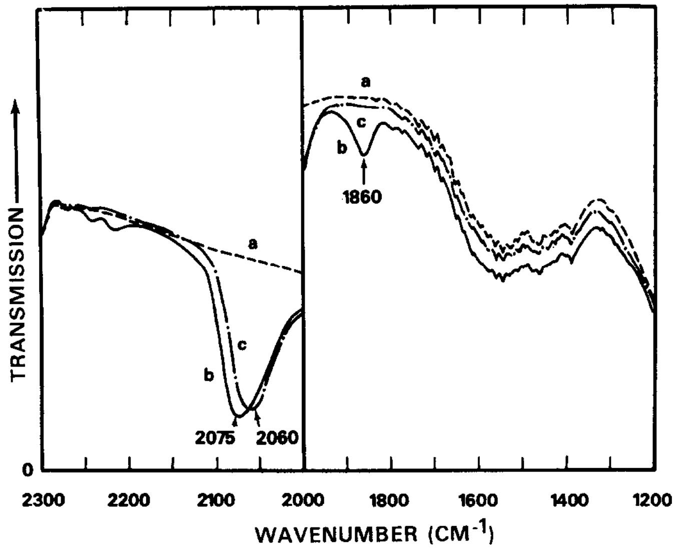

FIG. 2. Spectra of CO adsorbed on 0.8% Pt/Al_2O_3(X): (a) after reduction in H_2 at 400°C and evacuation at 500°C; (b) $a + 7.4$ Torr of CO; (c) after 5 min of evacuation.

Hydroxyl-stretching bands in the 3600–3800 cm^{-1} region and "carbonate" and/or "carboxylate" bands in the 1300–1700 cm^{-1} region, along with a "trapped CO_2" band at 2350 cm^{-1}, were normally seen in the spectra (*25–29*).

In the presence of added CO or NO additional infrared bands were seen, arising from CO or NO held by exposed Pt and/or Re atoms. The frequencies of the CO bands and the strength of attachment of the CO causing them were found to depend significantly on a number of factors, including pretreatment and reduction procedures. When, for example, fresh 0.8% Pt catalyst is merely evacuated at 400°C, with no reduction in H_2, and CO is subsequently added, bands are seen in the 2080 to 2130 cm^{-1} region, with a maximum near 2110 cm^{-1} as well as bands in the 1200–1900 cm^{-1} region characteristic of carbonate and bicarbonate structures. The added CO apparently either reacted with residual PtO to form CO_2 which then formed carbonates on the dry alumina surface or reacted directly with PtO to form $PtCO_3$. The relatively high frequency of the bands due to linearly adsorbed CO is consistent with the Pt atoms to which the CO is attached being strongly influenced by neighboring oxide or chloride (*23*, *30*).

As illustrated in Fig. 1, however, evacuation alone if carried out at 600°C on a fresh 0.6% Pt/Al_2O_3 catalyst can effectively reduce the platinum. The strong band near 2070 cm^{-1} is caused by CO linearly adsorbed on Pt, and the weaker band at 1865 cm^{-1}, not normally reported for CO on Pt catalysts, is probably caused by "bridged" CO (i.e., CO attached to two Pt atoms). No significant formation of new carbonates or bicarbonates was evident. This establishes that the catalyst was fairly completely reduced. The small bands above 2200 cm^{-1} represent CO held on sites on the alumina support (*26*).

Figure 2 shows spectra obtained for CO adsorbed on a fresh 0.8% Pt/Al_2O_3 catalyst after prior reduction in H_2 at 400° and evacuation at 500°C. Here again we see that added CO (7.4 Torr) produces a strong band at 2075 cm^{-1}, caused by linearly adsorbed CO, and a smaller bridged CO at 1860 cm^{-1}. Once again, no significant formation of surface carbonates or bicarbonate occurs, as evidenced by the lack of other new bands in the 1200–1900 cm^{-1} region. When the cell was evacuated to remove weakly adsorbed CO, which was apparently held mostly in the bridged form, the 1860 cm^{-1} band disappeared and a shift was seen in the linear CO band from 2075 to 2060 cm^{-1}. This suggests that the bridged CO affects the linearly held CO, implying that either the same or adjacent Pt atoms are involved as the adsorption sites. Bridged CO bands in the 1800 to 1840 cm^{-1} region have been reported for CO on Pt aggregates prepared from Pt carbonyl cluster compounds dispersed on γ-Al_2O_3 or silica gel (*31*).

"Titration" of reduced 0.6% Pt/Al_2O_3, with small known successive additions of CO and measurements of the very low residual gas pressures as spectra were recorded after each addition permitted calculation of an extinction coefficient for CO linearly adsorbed on Pt. This was found to be $2.4 \times 10^{-18}/cm^2$/molecule in essential agreement with results of previous studies (*21*, *22*). No shift was seen in the position of the CO band (2060 cm^{-1}) as CO was added until a coverage of roughly 0.7 CO molecule/Pt atom was reached (pressure $\sim 7 \times 10^{-3}$ Torr). At higher pressures, the band shifted to 2070 cm^{-1} without increasing appreciably in intensity.

Figure 3 shows spectra of CO adsorbed on the catalyst of Fig. 2 again reduced in H_2 at 400°C, but in this case subsequently heated to 800°C under vacuum and then held for 0.5 hr at 800°C during evacuation. The strong band at 2070 cm^{-1} now appears narrower than in Fig. 1 and exhibits little or no shift when the CO pressure is greatly reduced. The bridged CO band at 1860 cm^{-1} is weaker than in Figs. 1 or 2. That this band should be weaker after high-temperature evacuation, although the 2070 cm^{-1} band is not, may be explainable in terms of "rug" formation at 800°C, resulting from sintering of more highly dispersed Pt. The number of exposed Pt atoms available for linear adsorption of CO would not thereby be much reduced, but the number of edge Pt atoms, which might also bind a bridged CO molecule, would decrease markedly. Alternatively, a change in the type of crystal face preferentially exposed might also affect the rela-

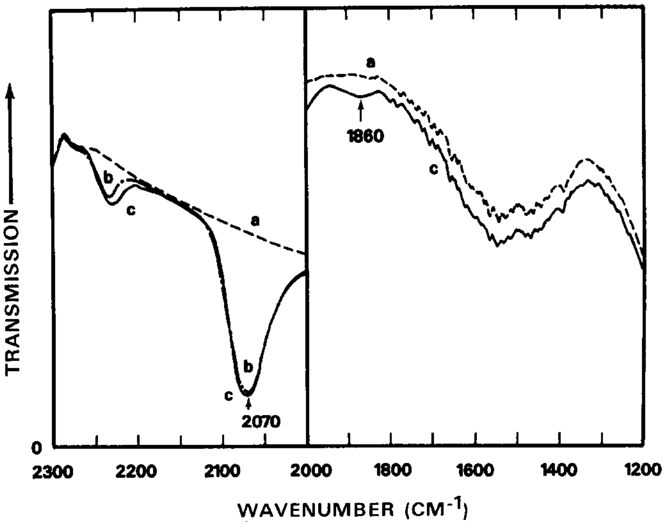

FIG. 3. Spectra of CO adsorbed on 0.8% Pt/Al_2O_3(X): (a) after reduction in H_2 at 400°C and subsequent evacuation at 800°C; (b) a + 1.35 Torr of CO; (c) a + 7.2 Torr of CO.

TABLE 2

Loss of Pt Area on Reduced Pt/Al_2O_3 Heated in O_2[a]

Catalyst	Pt (%)	Temperature (°C)	O_2 pressure (Torr)	% of original Pt area remaining (%)
X (fresh)	0.8	800	(Reduced)	90+
X (fresh)	0.8	800	Preoxidized[b]	35
Y (fresh)	0.6	600	200	44
B	0.6	600	200	26
B + 2 hr in Cl_2	0.6	600	200	39
E	0.6	600	200	20
E + 2 hr in Cl_2	0.6	600	200	32
E + 4 hr in Cl_2	0.6	600	200	30
F	0.4	600	200	32

[a] For 1 hr at 600°C or for 0.5 hr at 800°C after prior reduction, followed by another reduction.

[b] Preoxidized at 600°C, heated *in vacuo* at 800°C, then reduced.

tive ease of binding bridged CO molecules on a surface largely covered with linearly adsorbed CO.

When reduced Pt catalysts were heated in H_2 or *in vacuo* after H_2 reduction surface area loss appeared to be very slow, even at 700 or 800°C. Sintering is evidently not rapid on these catalysts in the reduced state. On the other hand, heating Pt catalysts in O_2 (after initial reduction) at 600°C invariably gave a major loss of Pt area (after rereduction at 600°C) in 1 hr.

TABLE 3

Loss of Pt Area on Heating Reduced 0.8% Pt/Al_2O_3 in O_2[a]

Catalyst	Temperature (°C)	Time (hr)	O_2 pressure (Torr)	% of original Pt area remaining (%)
A	500	1	760	90+
A	550	1	200	75
A	550	17	200	29
A (rejuvenated in $CCl_4 + O_2$)	600	1	200	34
C	400	16	200	95+
C	450	68	200	95+
C	500	4	200	90+
C	500	20	200	85
C	550	1	200	77
C	550	2	200	64
C	550	20	200	38
C	600	1	200	44
C (rejuvenated in Cl_2)	600	1	200	42
C	700	1	4×10^{-2}[b]	33
C	800	0.5	~0 (reduced)	90+

[a] Area measured after subsequent reduction.

[b] Preoxidized at 500°C in 200 Torr of O_2 for 1 hr.

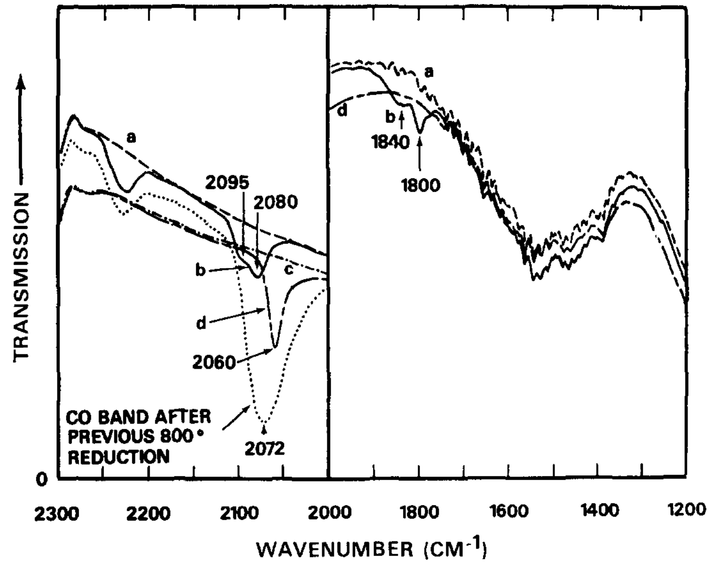

FIG. 4. Spectra of CO adsorbed on 0.8% Pt/Al_2O_3(X): (a) after heating in O_2 at 600°C and subsequent evacuation at 800°C; (b) *a* + 9.0 Torr of CO; (c) after subsequent reduction and evacuation at 400°C; (d) *c* + 8.0 Torr of CO.

As shown in Table 2, the fraction of the original area, indicated by the intensity of the linear CO band in the 2060–2080 cm^{-1} region, typically remaining after 1 hr in O_2 at 600°C ranged between 20 and 44%. The preservation of original area appeared greater on catalysts that had been more heavily treated with Cl_2 + air.

Table 3 shows additional data on the loss of Pt area resulting from heating used 0.8% Pt catalysts, reduced and in O_2, at temperatures between 500 and 800°C. Area is apparently lost at an increasingly rapid rate above 500°C.

Figure 4 illustrates the spectra obtained for adsorbed CO after heating fresh 0.8% Pt/Al_2O_3 catalyst in O_2 at 600°C, then under vacuum at 800°C for 0.5 hr, and again after rereduction and evacuation at 400°C in H_2. The substantial reduction in Pt area, indicated by the decrease in the (linear) CO band intensity as compared to that observed after the previous 800°C reduction in H_2, is seen to be accompanied by a frequency shift from 2072 to 2060 cm^{-1}.

The same behavior was observed on a rejuvenated used sample of this 0.8% Pt catalyst. The bands for adsorbed CO were closely similar to those already discussed. The exact frequency of the linear CO band near 2070 cm^{-1} depends on chloride level (*15*) and crystallite size. It is also affected by the degree of interaction with oxide or hydroxide ions in the support surface. High chloride shifts the band to higher frequency; large Pt crystals appear to give bands at lower frequencies (down to 2040 cm^{-1} or less).

The possible effect of H_2O vapor on Pt area was also briefly studied. Exposure to H_2O vapor (10 Torr) at 400°C normally eliminated acidic sites on the alumina or oxidized Pt sites which give CO bands from 2100 to 2240 cm^{-1} but only slightly decreased the Pt area shown by the band near 2070 cm^{-1}.

As indicated by the spectra in Fig. 5, the area lost by heating platinum catalyst at 600°C in O_2 was restored by heating the catalyst in CCl_4 + O_2 at 500°C or, as

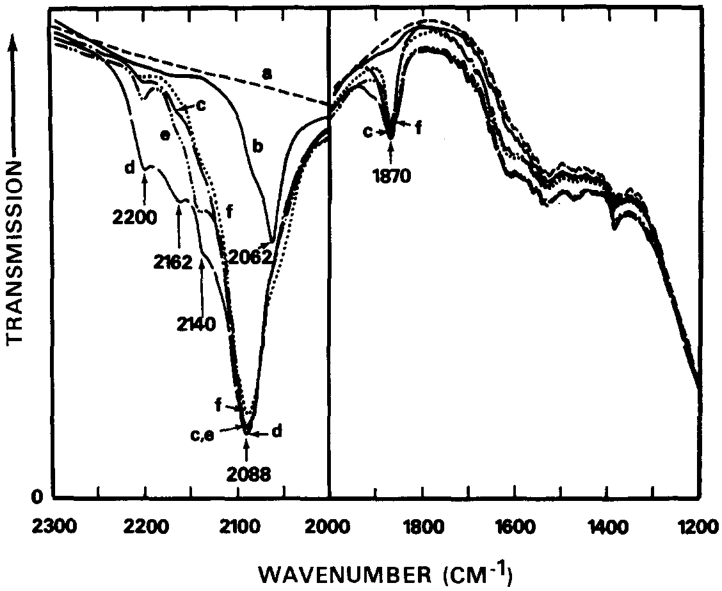

FIG. 5. Spectra of CO adsorbed on rejuvenated, used 0.8% Pt/Al_2O_3(A): (a) after heating catalyst in O_2 at 600°C and reducing at 500°C; (b) *a* + 8.0 Torr of CO; (c) after rejuvenation of catalyst by heating in CCl_4 + O_2 at 500°C, reduction in H_2 at 500°C, and addition of 8.0 Torr of CO; (d) *c* + 200 Torr of CO; (e) after evacuation to 0.025 Torr; (f) after evacuation to $<10^{-4}$ Torr.

shown in other experiments, by heating in wet Cl_2 + air. The degree of redispersion obtained—even on used catalysts which, as shown here, had seen many regenerations—was extremely high. The adsorption of CO on such catalyst approached one molecule per Pt atom. The influence of the high chloride level presumably present in these catalysts is apparently shown both by the unusually high frequencies (2088 and 1870 cm^{-1}) of the major CO bands and by stronger-than-normal binding of the bridged CO, which in this case was not removed by evacuation at room temperature. At higher CO pressures (curves d and e) evidence was seen for additional bands (2200, 2162, and 2140 cm^{-1}) similar to bands seen for chlorocarbonyl complexes of platinum (*30*).

Rhenium is considerably more difficult to reduce completely when held on alumina than is platinum. The argument has been made that it is not normally in a reduced state on an operating Pt–Re catalyst (*13*). Other evidence suggests, however, that it is at least substantially reduced (*14*). The conditions for most effective reduction are still not adequately understood, but in our experiments the extent of reduction seemed to depend markedly on pretreatment and aging. Preheating in O_2 at 600°C aided reduction. Aging of fresh catalyst made reduction more difficult. Generally both reduced and oxidized Re atoms existed on the surface of a pure alumina support after typical reduction in H_2 as also found by others (*17*), and these probably also exist under typical reforming conditions.

Figure 6 shows spectra obtained for CO adsorbed on a fresh catalyst holding 0.6% Re on alumina reduced in H_2 at 500°C and again after preheating in O_2 and reduction at 500°C. Similar, though somewhat stronger, bands were obtained on 1.2% Re/Al_2O_3 preheated in O_2 and reduced at 600°C. The main CO band, in both cases, appears around 2050 cm^{-1} with a small band near 2110 cm^{-1} caused by weakly held CO and another caused by strongly held bridged CO near 1960 cm^{-1}. The absence of carbonate or bicarbonate bands might be taken as an indication that the rhenium is completely reduced, but this would require showing, which has not been done, that such bands are produced when the Re is oxidized.

Figure 7 shows spectra of CO adsorbed on catalyst containing both Pt and Re after pretreatment similar to that given the Re/Al_2O_3 catalysts. The 600°C treatment in O_2 should have been adequate to reduce markedly the Pt area on Pt/Al_2O_3 and shift the CO band to 2060 cm^{-1} (see Figs. 4 to 6). The relatively sharp band at 2060 cm^{-1} in curve d appears to represent the CO/Pt band normally expected, superimposed on the usual CO/Re bands. The disappearance of the smaller band near 1860 cm^{-1} representing bridged CO on Pt and the persistence of the band (or shoulder) near 1950 caused by CO on Re also appears to be what would be expected if Pt area was lost through Pt crystal growth unaffected by the Re, which in turn behaved as expected for Re/Al_2O_3. It is clearly difficult to be sure, on the basis of the CO bands alone, whether or not some interaction is occurring. The spectra do indicate, however, that at least a substantial fraction of each metal is behaving as would be expected in the absence of the other.

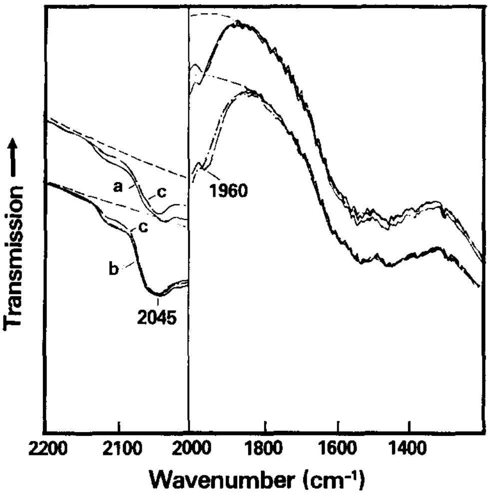

FIG. 6. Spectra of CO adsorbed on 0.6% Re/Al_2O_3: (a) after reduction in H_2 at 500°C and addition of 6.4 Torr of CO; (b) after heating in O_2, subsequent reduction at 500°C, and addition of 7.0 Torr of CO; (c) after 5 min of evacuation.

Figure 8 shows spectra typically obtained for adsorption of NO. As can be seen, adsorbed NO typically gives only one major band, at 1820 cm^{-1}, on reduced Pt/Al_2O_3. (No adsorption is seen on the alumina support.) On Re/Al_2O_3, however, two NO bands appear, at 1860 and 1780 cm^{-1}. Similar bands have been reported for NO adsorbed on Re/Al_2O_3 catalysts of much higher rhenium content (19 and 25% Re), but the adsorption sites in these cases represented only a small fraction of the rhenium (*16*). The bands were attributed to NO on partially oxidized Re ions generated by reduction of the catalyst. In the present case, with only 0.6% Re/Al_2O_3, the sites responsible for these bands apparently represent a major fraction of the Re if, as seems reasonable, the extinction coefficient for the adsorbed NO on Re is reasonably close to that on Pt. The apparent area of exposed Re, as evidenced by the intensities of the NO bands, did not seem to be affected (after subsequent reduction in H_2) by heating in O_2 at 600°C for 1 hr, but significant loss was observed after heating in O_2 at 700°C as shown by curve C in Fig. 8. In a typical experiment prereduced catalyst containing 0.6% Re/Al_2O_3, after heating for 1 hr in 200 Torr of O_2 at 700°C and subsequent reduction in 50 Torr of H_2 at 500°C, appeared to have lost about 50% of the Re area it exhibited after the original reduction in H_2 at 500°C. The reduction in the absorbance of the 1860 cm^{-1} band (41%) was, however, significantly less than that of the 1780 cm^{-1} band (63%). This indicates that two distinct types of Re sites exist.

The Re sites responsible for the 1860 cm^{-1} NO band are probably in a higher oxidation state than those causing the 1780 cm^{-1} band. Probably the former are exposed

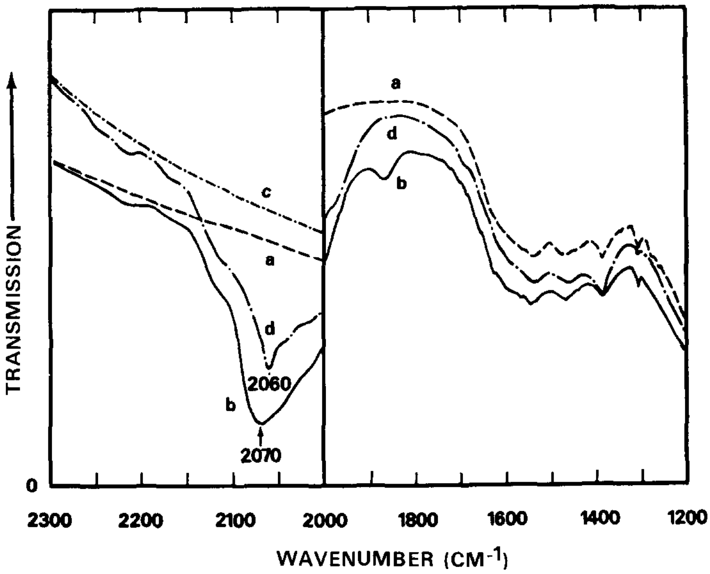

FIG. 7. Spectra of CO adsorbed on 0.5% Pt + 0.5% Re/Al_2O_3: (a) after reduction and evacuation at 500°C; (b) *a* + 7.2 Torr of CO; (c) after heating in O_2 at 600°C and reduction in H_2 at 500°C; (d) *c* + 7.6 Torr of CO.

Re^{4+} (*17*) ions, but possibly they represent Re in a still lower oxidation state. The 1780 cm^{-1} band could well be caused by NO held on reduced Re atoms (Re^0). The frequency of the band is certainly low enough to be consistent with adsorption on Re^0. The fraction of the total number of Re sites adsorbing to give the 1780 cm^{-1} band appears to be roughly half (as estimated from the band intensities assuming equal adsorptivities for NO on the two types of sites). This appears to be consistent with other data (*17*) indicating that, on reduced Re/Al_2O_3 catalysts containing 0.1 to 1% Re, 0.4 to 0.6 molecule of CO are strongly adsorbed per Re atom. The CO would not be strongly adsorbed on Re^{4+} ions, for example, but would on Re^0. One NO molecule might be held on each exposed Re^0 atom to give the 1780 cm^{-1} band.

The 1780 cm^{-1} NO band probably thus arises from NO adsorbed either on exposed Re^0 atoms or on Re ions in a low oxidation state (Re^{2+}?) produced by initial oxidation of Re^0 atoms by NO (i.e., $Re^0 + NO \rightarrow Re^{2+} O^{2-} + 0.5 N$). In either case, the band presumably reflects the number of Re^0 atoms initially exposed. Whether this is correct or not, the state of the exposed Re atoms seems to be reflected in the bands produced by adsorbed NO and changes in this state would presumably be shown by changes in the NO bands.

Figure 9 shows spectra of adsorbed NO obtained when both Pt (0.6%) and Re (0.6%) are held simultaneously on a reduced alumina-supported catalyst. Spectra shown on the left were obtained on fresh catalyst. Those on the right were obtained on a catalyst which had been run through 10 cycles of oxidation at 600°C, followed by wet Cl_2 + air at 500°C. When first adsorbed on reduced Pt–Re catalyst the NO bands apparently represent the sum of the individual sets of bands normally expected for NO on Pt/Al_2O_3 and for NO on Re/Al_2O_3 (curve a). When the catalyst is simply heated to 600°C during evacuation to remove NO, the Re is oxidized, as previously stated, and no longer adsorbs much NO. Thus, the bands seen in the b curves are largely those normally expected for NO adsorbed on Pt/Al_2O_3, with only a slight contribution from NO/Re bands. Heating the catalyst in O_2 at 600°C, as discussed previously, destroys most of the Pt area, but does not affect Re dispersion adversely. Thus, after the catalyst has again been reduced at 500°C in H_2 and NO has been added, we find that (curve c) the two NO bands resemble those expected for $NO/Re/Al_2O_3$. (A small NO/Pt band presumably underlies these bands.) After heating in O_2 at 700°C and rereduction the Re area has evidently decreased, as evidenced by the lower intensity of the NO bands in curve d, to the roughly same extent as would have been seen for Re/Al_2O_3 alone (see Fig. 8). Thus, as in the case of the CO bands, the NO bands apparently show that the Pt and Re sites on the Pt–Re catalyst behave independently, being destroyed and created just as if they were present alone on the alumina support. Subsequent treatment of $Pt–Re/Al_2O_3$ catalyst, which showed major loss of both Pt and Re areas after pretreatment in O_2 at 700°C, with wet Cl_2 + air at 600°C fully restored both the Pt and the Re areas to the values found after the original 500°C reduction.

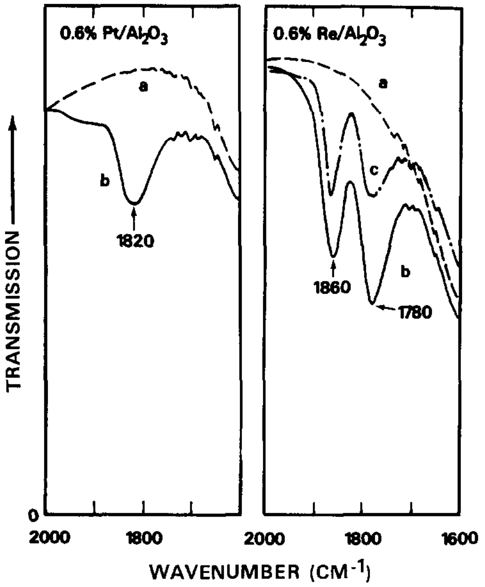

FIG. 8. Spectra of NO adsorbed on Pt/Al_2O_3 and on Re/Al_2O_3: (a) after reduction in H_2 at 500°C; (b) after addition of NO (~6 Torr); (c) after readdition of NO following heating of catalyst in O_2 at 700°C and reduction in H_2 at 500°C.

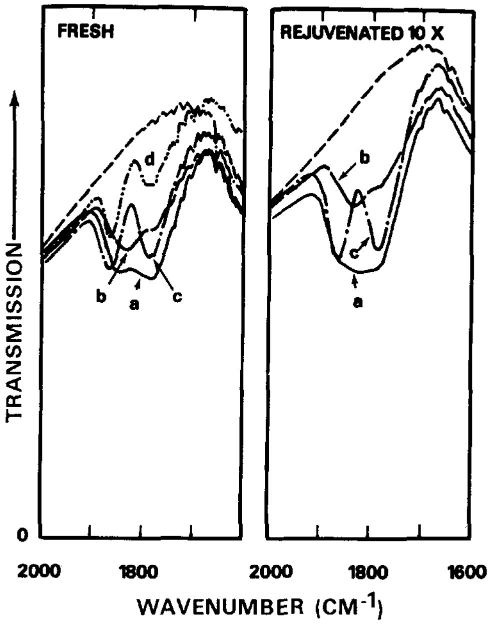

FIG. 9. Spectra of adsorbed NO on 0.6% Pt+0.6% Re/Al_2O_3: (a) NO added after 500°C reduction; (b) NO readded after 600°C evacuation; (c) after heating in O_2 at 600°C, reduction, and readdition of NO; (d) after heating in O_2 at 700°C, reduction, and readdition of NO.

That similar behavior is to be expected in prolonged service in refinery units is indicated by the spectra in Fig. 10. The spectra on the left represent NO adsorbed on a fresh $Pt–Re/Al_2O_3$ catalyst after reduction in H_2 at 500°C. Those on the right show spectra under similar conditions on the same catalyst taken from a refinery catalytic reforming unit after 59 regenerations. Although the spectra on the used catalyst at 6 Torr of pressure of NO exhibit some additional sharp bands (a complication apparently caused by NO on contaminant Fe ions), the spectra representing strongly adsorbed NO (curve b) appear to show that both Pt and Re possess the same general character on the

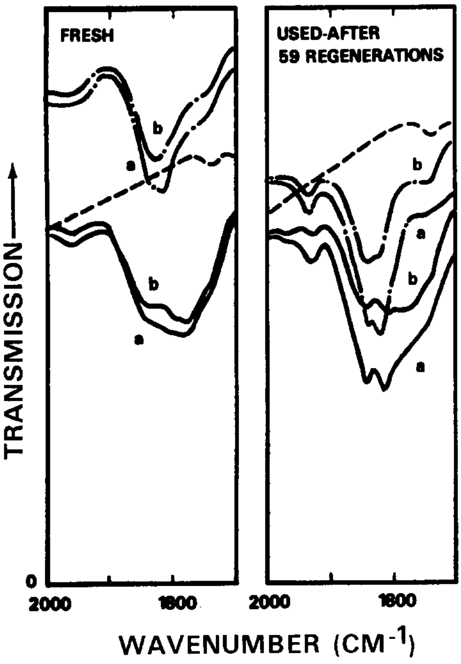

FIG. 10. Spectra of NO adsorbed on fresh and used 0.5% Pt–0.5% Re/Al_2O_3 catalyst: (——) NO added after reduction in H_2 at 500°C; (–··–) NO re-added after subsequent evacuation at 600°C. (a) Spectra, at ~6 Torr of NO; (b) spectra, after 5 min of evacuation.

used catalyst as on fresh catalyst. When unreduced Fe is a serious contaminant on used commercial catalysts, Pt and Re dispersions can be evaluated from study of CO bands.

CONCLUSIONS

Infrared study of adsorbed probe molecules obviously provides abundant evidence on the state of dispersion and the chemical nature of supported Pt and Re held on alumina at concentrations typical of those used in commercial reforming catalysts. While not all of this evidence can be unambiguously interpreted at present, the intensities and frequencies of bands due to adsorbed CO and NO can be used to demonstrate major interactions (or the lack thereof) between the supported metals or between metals and the support, reflecting such factors as the influence of neighboring oxide or chloride ions.

Platinum–rhenium catalysts are durable and can be regenerated and rejuvenated many times, apparently without significant change in the degree of dispersion or chemical nature of the supported metals. Although metal area is lost when catalyst is heated at high temperatures in oxygen, the lost area can be restored by treatments with Cl_2 + air or with CCl_4 + air. No significant loss of Re appears to occur under conditions likely to be encountered in commercial operation. No evidence was seen for formation of "alloys" or metallic clusters of Pt and Re atoms (or of Pt atoms with Re ions) wherein the electronic properties of one metal are altered by the presence of the other. The metals together apparently exhibit the adsorptive properties expected for the metals alone on an alumina support. This, of course, does not rule out the possibility that a small fraction of the metal may be involved in alloy or cluster formation.

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