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Adsorption of Carbon Monoxide on Platinum Alloys: An Infrared Investigation

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The effect of alloying on the absorption band frequency of CO adsorbed on Pt, $\tilde{\nu}$(CO/Pt), has been investigated with the alloys Pt–Pb, Pt–Sn, and Pt–Re. By use of the isotopic dilution method, it has been established that the downward shift of $\tilde{\nu}$(CO/Pt) observed upon alloying Pt with Pb is caused partly by a dilution effect and partly by another, possibly electronic effect. Alloying Pt with Sn or Re, on the other hand, caused only a small shift of $\tilde{\nu}$(CO/Pt), which, moreover, could also be explained at least partly by a dilution effect. Oxidation of the alloy samples resulted in a phase separation of the components; the alloy situation could be restored again by a reduction procedure.

INTRODUCTION

It is an exception rather than a rule that industrially applied catalysts contain only one active component. Usually several components with different functions are used, together with more or less active carriers and promoters.[2] Before a correct picture of the catalytic function of a multicomponent catalyst can be formed, several aspects must be considered and investigated. First, the chemical and structural composition of the surface must be known. In spite of considerable progress during the past decade, mainly due to the introduction and application of many new surface spectroscopic techniques, a quantitative surface analysis of supported, low-loaded catalysts is still further away than is desirable. Second, once the surface composition is known, the role of all individual components should be established. The mere presence of a species in or on the surface does not automatically imply its catalytic relevance.

Supported alloys are an example of multicomponent catalysts, known and applied for some time already. Catalysts used in hydrocarbon conversion processes usually consist of platinum with one or more additional components, dispersed on an oxidic support. Among the additives are, e.g., Ge, Ir, Pb, Sn, and Re. The support most commonly used is γ-alumina. Usually the function of the additional components is to improve either the selectivity or the stability of the catalysts.

The variations in catalytic activity by alloying have often been ascribed to changes in the electronic structure of the active component(s). A major argument to support this interpretation was the information obtained from the ir spectra (mainly the shift in the absorption band frequency) of CO adsorbed on the active metal, e.g., Pt. This frequency decreased with increasing dilution by the second component. The proposed explanation was that an increased electron concentration on Pt, caused by the second metal, would increase the extent of back-donation into the antibonding 2π-orbitals of CO. This would reduce the C–O bond strength and thus its absorption band frequency $\tilde{\nu}$(CO/Pt). However, by using the so-called Isotopic Dilution Method (*1*), we have shown that this is not as common a

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[2] A convenient definition of a promoter is that it is a compound which, although inactive itself, improves one of the catalytic aspects of the component(s), e.g., activity, selectivity, surface area, pore structure, stability.

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phenomenon as was once supposed. With the system Pt–Cu, the whole effect of Cu on $\tilde{\nu}$(CO/Pt) could be ascribed to the dilution effect of Cu on Pt (*2*). Alloying causes an increased distance between the CO molecules on Pt atoms, and thus a reduced dipole–dipole coupling between these CO molecules. An electronic effect, if it exists at all, is below the detection limits of our ir experiments (*2*). On the other hand, the system Pt–Pb showed clearly larger frequency shifts of $\tilde{\nu}$(CO/Pt) (*3, 4*). The isotopic dilution method revealed that in this case only a part of the total effect could be ascribed to a dilution effect of Pb on Pt (*4*). This has led us to the idea that the exothermicity of the formation of the alloy under consideration might be an important parameter: Pt–Pb alloys (*6*) are formed with a higher exothermic effect than Pt–Cu alloys (*5*).

In this paper, results are presented on a series of Pt–Pb alloys. An attempt is made to obtain a more complete picture of this system with regard to the chemisorption of CO. Further, the behavior of one Pt–Sn and two Pt–Re alloy samples have been investigated. Pt–Sn is formed more exothermically than Pt–Pb (*7*), but Pt–Re is probably formed without any thermal effect at all (*8*). We have also investigated the effect of pretreatment of the samples, in particular that of oxidation (with or without subsequent reduction) on the absorption band frequencies.

EXPERIMENTAL

A series of Pt–Pb alloys, one Pt–Sn, and one Pt–Re alloy were prepared by homogeneous precipitation with urea (*9*). Lead was used in the form of $Pb(NO_3)_2$ (spec. pure, Aldrich) in water. Tin (spec. pure, Drijfhout, Amsterdam) was dissolved in as little aqua regia as possible. Rhenium (spec. pure, Drijfhout, Amsterdam) was dissolved in as little nitric acid as possible. For further details, see the Refs. (*1, 4, 10*). A second Pt–Re sample was put at our disposal by Professor G. Leclercq (Université de Lille, France). It contained 37.5 at% Pt and will be denoted hereafter in the terminology of Professor Leclercq as Pt–Re (PRD 62.5). This sample was prepared by coimpregnation. In all cases γ-alumina was used as the support and the total metal loading was 5 wt% (see also (*11*)).

Details of the procedures applied, such as X-ray fluorescence (*2*), ir spectrometry (*1, 10*), and adsorption measurement (*12*) are presented in the literature quoted.

A series of Pt–Pb alloys has been prepared with 96, 88, 73, 41, and 18 at% Pt in the bulk, as determined by X-ray fluorescence. All samples had a particle size smaller than 20 Å as estimated from the absence of X-ray diffraction patterns and from electron micrographs.

Similarly as with the Pt–Cu system (*2*), the frequency of the absorption band maximum of CO adsorbed on Pt (at full Pt surface coverage) is reduced upon alloying with Pb. In Fig. 1, the wavenumber of this band is plotted as a function of the bulk alloy composition. The dotted line is the analogous plot for the Pt–Cu system (*10*). From this figure, it is clear that the effect of Pb is much larger than that of Cu.

In order to investigate the nature of the effect of Pb, we performed isotopic dilution experiments as described earlier (*1, 2, 4, 12*). In Fig. 2 the wavenumbers of the high-frequency bands of all alloys and unalloyed Pt (the dotted line, taken from Ref. (*1*)) are

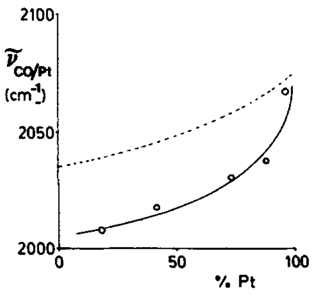

FIG. 1. Wavenumbers of the ir absorption band maxima of adsorbed CO as a function of the alloy composition of $Pt\text{–}Pb/Al_2O_3$ alloys. The dotted line indicates the analogous curve for the Pt–Cu system (*2*).

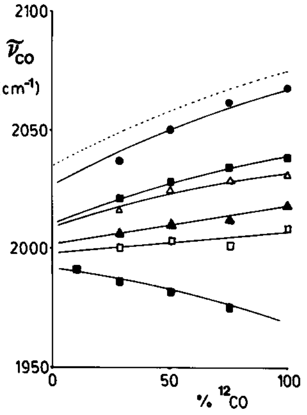

FIG. 2. Wavenumbers of the ir absorption band maxima of adsorbed (^{12}CO/^{13}CO) mixtures as a function of the isotopic composition of the adsorbed layer for the Pt-Pb/Al$_2$O$_3$ alloys. ●, Pt-Pb 96-4; ■, Pt-Pb 88-12; △, Pt-Pb 73-27; ▲, Pt-Pb 41-59; □, Pt-Pb 18-82. The dotted line indicates the analogous curve for Pt/Al$_2$O$_3$ (*1*). For reasons of clarity the low-frequency band points are omitted with the exception of those for the Pt-Pb 88-12 sample, to indicate the comparable behavior.

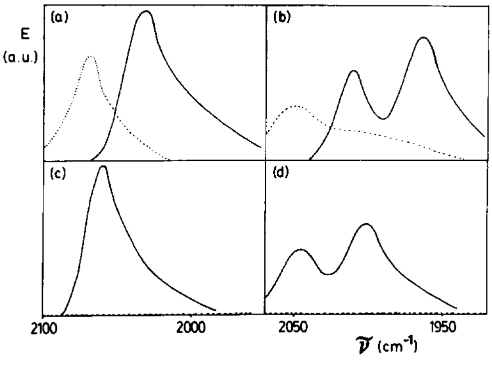

FIG. 4. Spectra of CO adsorbed on Pt-Pb 41-59 and Pt-Sn 50-50. The effect of oxidation. (—) Reduced sample; (· · ·) oxidized sample. (a) ^{12}CO on Pt-Pb 41-59; (b) ^{12}CO/^{13}CO 50/50 on Pt-Pb 41-59; (c) ^{12}CO on Pt-Sn 50-50; (d) ^{12}CO/^{13}CO 50/50 on Pt-Sn 50-50.

plotted as a function of the isotopic composition of the adsorption layer. It is clear that upon infinite dilution of ^{12}CO by ^{13}CO a part of the effect of Pb on $\tilde{\nu}$(CO/Pt) persists which cannot be ascribed to dilution. This residual effect, additional to the dilution effect, grows with the amount of Pb in the alloy, as can be seen in Fig. 3.

Further, one Pt-Sn and two Pt-Re samples were investigated. All these samples had approximately equal amounts of both alloy components. The particle sizes of all samples were again below the detection limit of X-ray diffraction.

In Fig. 4 it can be seen immediately that the effect on $\tilde{\nu}$(CO/Pt) of alloying Pt with Pb (Fig. 4a) is much larger than that of alloying Pt with Sn (Fig. 4c). Both Pt-Re samples behave similarly to Pt-Sn, in this sense. In Fig. 5 the results of the isotopic dilution experiments on Pt-Re and Pt-Sn are shown together with those obtained with unalloyed Pt (the dotted curve). It can be seen that the effect of both Sn and Re on $\tilde{\nu}$(CO/Pt) is partly caused by a dilution effect, but a small "extra effect" of 5-10 cm^{-1} cannot be a priori excluded.

The effect of sample pretreatment, i.e.,

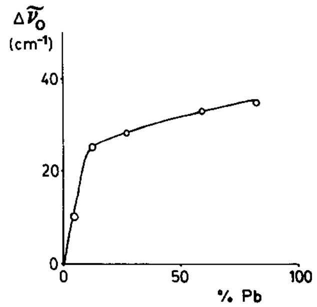

FIG. 3. The additional effect of Pb on $\tilde{\nu}$(^{12}CO/Pt), i.e., without the dipole-dipole coupling effect, as a function of the alloy composition.

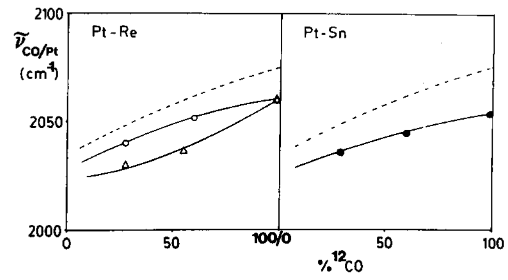

FIG. 5. Wavenumbers of the high-frequency bands as a function of the isotopic composition. ○, Pt-Re 50-50. △, Pt-Re (PRD 62.5). ●, Pt-Sn 50-50.

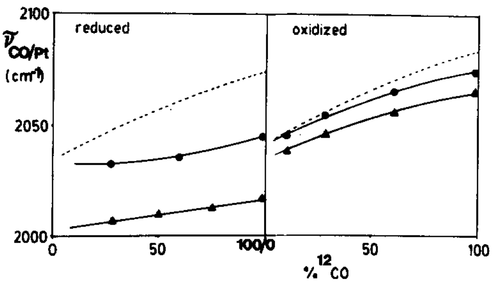

FIG. 6. Wavenumbers of the high-frequency bands as a function of the isotopic composition. The effect of pretreatment, i.e., oxidation with or without subsequent reduction. ●, Pt–Cu 31–69 (see also Ref. (*2*)); ▲, Pt–Pb 41–59.

the effect of oxidation, with or without a subsequent reduction, appeared to be rather surprising. With Pt–Cu and Pt–Pb supported alloys, absorption band frequencies were found, almost equal to that of unalloyed Pt, as can be seen in Figs. 4a, b, and 6. On the other hand, after oxidation, the Pt–Re and Pt–Sn samples did not show any CO adsorption at all. The results of isotopic dilution experiments on the oxidized Pt–Cu and Pt–Pb samples are shown in Fig. 6, together with the curve for oxidized Pt (the dotted line). The small effects of both Cu and Pb on $\tilde{\nu}$(CO/Pt) may be (almost) fully ascribed to a dilution effect.

As pointed out earlier (*2*), another important phenomenon, observable in the ir spectra of isotopic mixtures ^{12}CO/^{13}CO is the so-called transfer of intensity ΔI. By this term, one indicates that the high-frequency (or ^{12}CO-like) band in the spectrum is more intense (compared to the low-frequency band) than one would have expected according to the molar ratios of ^{12}CO and ^{13}CO. We define the intensity transfer ΔI, as earlier (*2*):

$$\Delta I = \frac{I(^{12}\mathrm{CO})}{I(^{13}\mathrm{CO})} \cdot \frac{X(^{13}\mathrm{CO})}{X(^{12}\mathrm{CO})}$$

In this equation, I denotes the intensity (or maximum extinction) of the ir absorption band and X the molar ratio of the respective species.

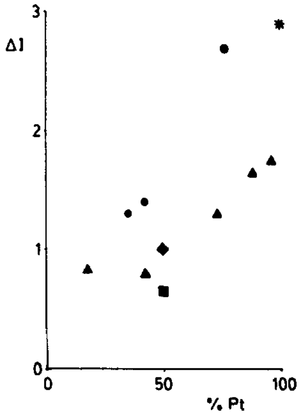

FIG. 7. Transfer of intensity ΔI in a 28/72 ^{12}CO/^{13}CO mixture as a function of the alloy composition. *, Unalloyed Pt; ●, Pt–Cu (2); ▲, Pt–Pb; ■, Pt–Sn; ◆, Pt–Re.

In Fig. 7, ΔI is plotted as a function of the bulk composition of the alloys investigated. Obviously, ΔI is strongly reduced by alloying. The transfer of intensity was shown to be affected also by the composition of the adsorption layer (*2*): ΔI increased upon decreasing content of ^{12}CO. This is confirmed again by the new experiments, as can be seen in Fig. 8. Besides this, ΔI is also affected by the oxidation state of the metal. After oxidation of the samples, ΔI is always larger than after reduction. As can be seen in Fig. 8, this increase is largest for the alloys.

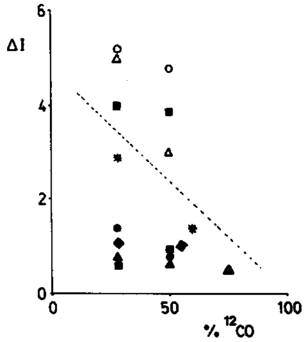

FIG. 8. Transfer of intensity as a function of the isotopic composition of the adsorbed layer. ●, Pt–Cu 42–58 reduced; ○, Pt–Cu 42–58 oxidized; ▲, Pt–Pb 41–59 reduced; △, Pt–Pb 41–59 oxidized; ■, Pt–Sn 50–50 reduced; ◆, Pt–Re 50–50 reduced; *, Pt reduced; ⊠, Pt oxidized.

TABLE 1

Adsorption Experiments

Sample	H/Pt	CO/Pt	$I_{CO}{}^{a}$ (cm^{-1})	$\bar{\varepsilon}_{mol}{}^{b}$ ($\times 10^{-6}$ cm^{-1}mol^{-1})
Pt	0.84	0.69	43	4.85
Pt–Pb 41–59	0.03	0.14	7	7.65
Pt–Sn 50–50	0.016	0.07	9	15

[a] Intensity of the ir absorption band of adsorbed CO $\int E_\nu \, d\nu$ in which $E = \log(T_{background}/T_{ads})$. $T_{background}$ stands for transmission with a clean adsorbate free surface, and T_{ads} transmission with an adsorbed layer.

[b] The $\bar{\varepsilon}_{mol} = I_{CO}/n_{CO}$ in which n_{CO} is the number of adsorbed CO molecules according to CO adsorption measurements.

Further, some independent adsorption measurements have been performed with one Pt–Pb and the Pt–Sn sample, in order to obtain information on the extinction coefficient, as described earlier (*12*). The results are shown in Table 1.

DISCUSSION

In an earlier paper (*2*), we have shown that alloying platinum with copper did not induce any additional electron transfer between platinum and adsorbed carbon monoxide, contrary to various earlier suggestions in the literature (*13*). By use of the isotopic dilution method, we could show that the absorption band frequency of CO adsorbed on Pt, $\tilde{\nu}$(CO/Pt), remained unchanged upon alloying, provided the dipole–dipole coupling effects were eliminated. By the same method, however, we have shown (Refs. (*2, 4*) and this paper) that at least with alloys of Pt and Pb, a part of the observed frequency shift caused by alloying (see Fig. 1) could not be ascribed to a reduced dipole–dipole coupling (or dilution) effect (see Figs. 2 and 3).

Alloys of Pt and Pb are formed with a stronger exothermic effect than Pt–Cu alloys: −27 kJ/mol (*5*) vs −10 kJ/mol (*6*) for 50/50 alloys. Consequently, a more pronounced "electronic structure" (or "ligand") effect might not be really surprising. One would expect, then, that in this case the shift of the frequency additional to that due to the coupling effect (i.e., the difference on the left side $\Delta\tilde{\nu}_0$ between the isotopic dilution curves, as in Fig. 2) would be larger or at least comparable for an alloy which is formed more exothermically, as Pt–Sn: −50 kJ/mol (*7*). In this model, an alloy such as Pt–Re, which is probably formed without a thermal effect (*8*), should behave like Pt–Cu. However, all results point out that such a trend ($\Delta\tilde{\nu}_0 \sim$ exothermicity) is not observed. The effects of Sn and Re are comparable and both are much smaller than that of Pb.

Table 2 summarizes the data which are relevant for the discussion. As far as the effect of alloying on the reduced samples is

TABLE 2

Summary of Relevant Thermochemical and Spectroscopic Data

Alloy 50–50	ΔH_f (kJ/mol)	I. Reduced			ΔI^{d}	II. Oxidized			ΔI^{d}
		$\Delta\tilde{\nu}_{100}{}^{a}$	$\Delta\tilde{\nu}_0{}^{b}$ (cm^{-1})	$\Delta\tilde{\nu}$(% ^{12}CO)^{c}		$\Delta\tilde{\nu}_{100}{}^{a}$	$\Delta\tilde{\nu}_0{}^{b}$ (cm^{-1})	$\Delta\tilde{\nu}$(% ^{12}CO)^{c}	
Pt–Cu	−10(5)	25	0–3	15	1.4	10	0	35	3.1
Pt–Pb	−27(6)	55	30	15	0.7	15	5	35	2.8
Pt–Sn	−50(7)	20	0–5	25	0.6	—	—	—	—
Pt–Re	0(8)	15	0–10	25	1.0	—	—	—	—

[a] The frequency shift of $\tilde{\nu}(^{12}CO)$ caused by alloying.

[b] The frequency shift by alloying at infinite dilution by ^{13}CO.

[c] The frequency shift of $\tilde{\nu}(^{12}CO)$ due to dilution by ^{13}CO.

[d] The intensity transfer $= \dfrac{I(^{12}CO)}{I(^{13}CO)} \times \dfrac{\%^{13}CO}{\%^{12}CO}$.

concerned, two possible explanations emerge immediately. Either the frequency without coupling effects is *not* related to the exothermicity of the alloy formation at all, or this relation does exist, but the Pt–Sn sample used is a less perfect alloy. It should be noted here, however, that to our knowledge appreciably lower $\tilde{\nu}$(CO/Pt) values have never been observed with Pt–Sn or Pt–Re alloys.

Regarding the alloy formation, several questions may be posed:

1. Has a real alloy been formed in the case of Pt–Sn and Pt–Re?

There are several indications that this is indeed so: (i) the integrated absorption band intensities in the ir spectra of CO adsorbed on all alloys are much smaller than that observed with unalloyed Pt, whereas the particle size of all samples is comparable. This means that the surface of the particles is not formed by Pt only. (ii) The reduction of $\tilde{\nu}$(CO/Pt) caused by alloying of Pt with Sn or Re is (partly) caused by a dilution effect (see Fig. 4a); (iii) Hydrogen and carbon monoxide adsorption experiments showed that the ratio H/CO was smaller for Pt–Sn than for unalloyed Pt (see Table 1). As Verbeek and Sachtler (*14*) have pointed out already, hydrogen possibly needs a larger ensemble of Pt atoms for its dissociative adsorption than carbon monoxide for its molecular adsorption. By alloying, the average ensemble size of Pt is most likely reduced. (iv) The transfer of intensity has been shown (both in the present work and in the earlier study (*2*)) to be reduced by alloying. For all (reduced) alloys, ΔI is clearly smaller than for unalloyed Pt (see Fig. 6). (v) On oxidized Pt–Sn and Pt–Re, CO was not adsorbed at all. Such behavior has never been observed for unalloyed Pt. The conclusion is obvious: Sn and Re are evidently influencing the Pt sites.

2. What is the degree of reduction of the alloy components (supported by an oxide) and could that influence the results?

An incompletely reduced component may be expected to have a decreased tendency to donate electrons to the other alloy component. One might speculate then that this could cause the smaller size of the expected "extra" (i.e., "ligand") effect $\Delta\tilde{\nu}_0$ in the ir spectra of CO on Pt–Sn and Pt–Re (see Fig. 4). Literature reports show that Sn and Re may indeed be deposited on the carrier in an ionic state and can be reduced to the metallic state only at rather high temperatures (>400°C). However, it is also known from the literature that when Sn or Re are alloyed with Pt, reduction is much easier. With the Pt–Re system, reduction may even be complete below 200°C (*16*). In view of this, it seems unlikely that, e.g., Re would have been incompletely reduced in our samples with 5 wt% metal loadings. However, since we had no independent means to establish the degree of reduction, we cannot fully exclude this effect either. Nor could the presence of separated (un)reduced Sn or Re on the carrier be detected, but, although catalytically perhaps interesting, such species will probably have no influence on the alloy particles, except that the ratios Pt/Sn and/or Pt/Re are larger in the alloy particles than the average ratios in the sample. However, this would not explain the strong reduction of electronic effects, since the conclusion of the discussion on question 1 was that Sn and Re were present all in fair amounts in the alloy particles.

3. May alloying have an influence on the particle size and through that on $\tilde{\nu}$(CO/Pt)?

Some suggestions in the literature indicate an effect of alloying on the particle size indeed (*17*). Furthermore, in a previous paper (*12*) we have shown with supported iridium samples that variations in particle size influence the absorption band frequency of adsorbed CO. Increasing the particle size increases the relative population of CO molecules (with a higher absorption band frequency) adsorbed on planes, as compared with those adsorbed on edges, corners, etc. With the iridium samples also, a particle size increase is accompanied by a decrease of the apparent average molar extinction coefficient, which may be related to the strength and the length of the metal–carbon bond (*12*). Therefore, one might speculate now on a pronounced particle size effect in the Pt–Pb system. An "extra" reduction of the frequency would be expected if the metal particles in this system were considerably smaller than with the other alloy systems. However, there are several arguments against such a speculation. First, it is unclear why just Pb and not Cu, Sn or Re would exclusively cause a decreased particle size. Second, electron micrographs did not reveal a significantly different particle size for Pt–Pb alloys, although a number of particles might have been too small to be observed. A third argument is based on the value of the apparent average molar extinction coefficient $\bar{\varepsilon}_{\mathrm{mol}}$. Although the proportionality between this empirical parameter and the adsorption bond strength may be questioned, it should nevertheless be expected that a pronounced particle size effect would affect $\bar{\varepsilon}_{\mathrm{mol}}$ in the same sense as in the case of iridium. As can be seen in Table 1, no exceptionally high value of $\bar{\varepsilon}_{\mathrm{mol}}$ is found for Pt–Pb. In fact, $\bar{\varepsilon}_{\mathrm{mol}}$ increases in the sequence Pt, Pt–Pb, Pt–Sn. Therefore, since there is no independent argument in favor of a significantly smaller average particle size of Pt–Pb samples, this speculation has to be rejected.

In view of all this, the ir results on CO adsorbed on the series of Pt–Pb alloys are most probably to be explained by some still unidentified electronic structure effect, which is not operating, or at least is much less pronounced, with Pt–Cu, Pt–Sn, and Pt–Re alloys. This electronic structure effect manifests itself mainly in the region of 0–20% Pb (see Fig. 3). A thorough investigation of catalytic reactions with Pt–Pb alloys should reveal the relevance of such an effect, i.e., a possibly different behavior as compared to alloys which lack this effect.

The effect on $\tilde{\nu}$(CO/Pt) of oxidation (without subsequent reduction) is quite dramatic, as can be seen in Figs. 4 and 5 and in Table 2. For Pt–Cu and Pt–Pb, the frequency shift due to the dilution by ^{13}CO, as well as the intensity transfer ΔI, are both strongly *increased*. Furthermore, the additional frequency decrease of $\tilde{\nu}$(CO/Pt) caused by Pb (see Figs. 2 and 3) is no longer present.

At the moment we are not able to offer a full explanation supported by independent experimental data. Our tentative explanation is as follows. Oxidation causes a corrosive separation of the alloy components, by the formation of oxidic clusters. When CO is admitted, the platinum oxide is quickly reduced by CO and the subsequent adsorption of CO on this Pt resembles that on unalloyed Pt samples. The integrated absorption band intensity of CO is not higher than on the reduced samples, which indicates that a real three-dimensional phase separation has not taken place. This is corroborated by the fact that a reduction procedure restores the original situation of the reduced sample, with the corresponding frequencies and intensities upon adsorption of CO.

It should be mentioned that a separation of alloy components has already been observed with Pt–Pd (*18*) and Pt–Au (*19*) alloys. With these systems, however, a reduction procedure did *not* restore the original situation. This could be related to the fact that these alloy systems are much less exothermic (in contrast with Pt–Cu and Pt–Pb), which reduces the driving force of alloy formation.

After oxidation of the Pt–Sn and Pt–Re samples, CO could not be adsorbed at all. Obviously, all platinum atoms have become unable to adsorb CO. The most likely explanation is that the alloy particles are covered by a tin oxide or rhenium oxide layer, or, in other words, Sn and Re are strongly enriched in the alloy surface by the action of oxygen. However, also in this case, a reduction procedure restores the original situation.

Summarizing, under oxidizing conditions, alloys may suffer phase separation, while the active metal (or its oxide) may even "disappear" into the bulk of the particles. From this it is clear that one should be very careful in extrapolating results obtained with reduced alloys to catalytic reactions in which strongly corrosive gases (like water) are present.

CONCLUSIONS

1. With the help of the isotopic dilution method it has been shown that the decrease of the absorption band frequency of CO adsorbed on Pt, alloyed with Cu, Sn, or Re, can be (almost) fully explained by a dilution effect. Alloying Pt with Pb shows an additional effect which might be related to an electronic structure effect. The reason why at least Sn does not show such an effect is not clear.
2. If the additional ("electronic") effect observed in the Pt–Pb system were to affect the catalytic behavior, the largest changes should be expected upon the addition of the first 20% of Pb to Pt.
3. Oxidation of the Pt–Cu and Pt–Pb alloys results in a partial phase separation. After reduction, the alloy particles are restored. Oxidation of the Pt–Sn and Pt–Re alloys causes Pt to disappear from the surface (or anyhow to become unable to adsorb CO). Reduction restores the original alloy particles.
4. The specific catalytic behavior of alloys like Pt–Sn and Pt–Re in hydrocarbon conversion processes is probably not caused by an electronic structure change of Pt. The reason of the superiority in selectivity and stability of these alloys is probably a combination of a dilution effect of platinum with a separate activity of the second metal.

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