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Infrared Studies of CO Adsorbed on Supported Pt–Co Catalysts

M. J. DEES,* T. SHIDO,† Y. IWASAWA,† AND V. PONEC*

**Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands; and*
†University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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The IR spectra of CO adsorbed on aerosil-supported Pt, Co, and several Pt–Co bimetallics have been investigated. It is observed that the addition of Co to Pt causes a decrease in the IR band wavenumber from 2075 to 2040 cm^{-1} at a given coverage θ(CO). A decrease in the coverage θ(CO) of the Pt and Pt–Co bimetallic surfaces also gives rise to a red shift, down to 2040 cm^{-1}. For this reason the effect of Co can be regarded as a geometric effect (dilution of the CO layer). The addition of Co to Pt results in the appearance of a second absorption maximum (above 2000 cm^{-1}) at 2086–2083 cm^{-1}. This maximum disappears relatively quickly following pretreatment in *n*-hexane. It is ascribed here to the adsorption of CO on smooth surfaces. The monometallic Co system differs considerably from the other systems in that (a) its surface is not blocked easily by *n*-hexane and (b) passing CO at elevated temperatures results in the formation of CO–carbonyl species. In the bimetallic catalysts no Co with this behavior (unalloyed Co) could be detected.

INTRODUCTION

Most commercial catalysts contain more than one component. For example, naphtha-reforming catalysts are "bimetallics." In addition to Pt and the support, they can contain other elements such as Ir (*1*), Re (*2*), and Sn (*3*). Bimetallics exhibit catalytic properties which are very different from those observed on single metals. The reason for this is the subject of ongoing research. Possible explanations include: changes through the formation of alloys (formation of bimetallics) which can be related to changes in electronic structure (*3–5*) or effects (on the reaction followed or on the side reactions) related to the size, structure, and composition of the reaction site (ensembles of surface atoms) (*6*).

The Pt–Co bimetallic system has already been studied in this laboratory (*7*) in hydrocarbon/hydrogen reactions in order to compare the experimental results with those obtained with Pt–Ir (*8*) and Pt–Re (*9*) systems. Cobalt, like Ir and Re, shows a pronounced hydrogenolytic activity: silica- and alumina-supported Co catalysts can achieve an almost 100% selectivity to methane in the *n*-hexane/hydrogen reactions. When the sulfur-free bimetallic catalysts (Pt–Re, Pt–Ir, Pt–Co) are tested in a catalytic reaction, a rather smooth and continuous change is observed between the behavior of Pt and that of the other metal. An increase in the Ir, Re, or Co content of the catalyst increases the selectivity to hydrogenolysis.

Catalytic results obtained in our laboratory did not show features which could be ascribed to "electronic structure effects" (N.B. catalytic data alone are never the best indication of the occurrence of such effects). However, Zyade *et al.* (*10*) claim that there are important electronic structure effects for the Pt–Co systems. Obviously, additional information on the Pt–Co system is necessary for a better understanding.

With the bimetallic Pt–Co system one can, in principle, expect alloy particles (*7*), unalloyed metals, unreduced metal ions, and a modified support (silica) to be present under the conditions of the catalytic experiments. Moreover, the presence of the other

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metal can alter the surface morphology of the metal in question in a way similar to that observed for metal films (*11, 12*). With this potential complexity, it is highly desirable to check which species manifest themselves in the chemisorption of gases. There are only a very few methods which are comparable to chemisorption in their sensitivity to surface sites. For this reason we hope to obtain additional information through the use of a suitable probe molecule. For the Pt–Co system, CO is quite promising.

Infrared spectra of CO adsorbed on supported Pt show (when compared at full coverage) a strong absorption maximum around 2070–2075 cm^{-1} (singly coordinated CO, "on top") (*13–15*) with a second band at about 1880 cm^{-1} (multiply bound CO). Alloying of Pt leads to a shift in the position of the absorption band. This shift to lower frequencies ("a red shift") increases with a decreasing Pt/(second component) ratio. For example, Toolenaar *et al.* (*15*) studied this effect by alloying Pt with Cu and observed that increasing the Cu content in the silica-supported Pt–Cu system resulted in a decrease in the band wavenumber from 2075 cm^{-1} (CO adsorbed on pure Pt) to 2040 cm^{-1} (CO adsorbed on Pt/Cu = 5/95).

In general, the red shift observed is ascribed either to a geometric or to an electronic effect. As to the electronic effect the suggestion has been made that the addition of the second component increases the back-donation of electrons of the metal (*d*-electrons) into the antibonding 2π-orbital of the adsorbed CO (*4*). This shift of electrons would weaken the C–O bond and would explain the observed red shift. However, several Pt alloys, which have been investigated in detail by Toolenaar *et al.* (*16, 17*), showed red shifts which could be attributed mainly to a simple dilution effect of Pt by the second component. In these studies (*16, 17*), mixtures of $^{12}CO/^{13}CO$ were adsorbed on the alloys and the $\tilde{\nu}(CO)$ was monitored. On monometallic Pt (*15*) approximately the same red shift (with respect to $\theta(CO) \rightarrow 0$) is achieved for the highest dilution of ^{12}CO (about 35 cm^{-1}) by ^{13}CO, as achieved by the highest dilution of Pt alloyed with either Cu, Sn, or Re. This fact by itself indicates that there is almost no room for the operation of a potential electronic structure (ligand) effect. Only the Pt–Pb alloys show an effect which is larger than the dilution effect (*4, 17*). The exothermicity of the Pt–Co alloy formation is not particularly high: for a 50/50 alloy it is −9.8 kJ/mol (*18*) compared to − 10 kJ/mol for Pt–Cu alloys (*19*). This does not lead us to expect large ligand effects (visible with the singleton frequency, $\tilde{\nu}(CO)$ for $\theta(CO) \rightarrow 0$) with the Pt/Co system. On the other hand Co exhibits a high affinity to CO (carbonyls are easily formed) than, e.g., Cu and the presence or absence of the "ligand" effect of alloying must be checked.

Knowing what the Pt–Co alloys can be used for, we decided to also take a brief look at the effects of coke/carbide formation. For example, the deactivating behavior of Pt–Co catalysts in *n*-hexane/hydrogen reactions appeared to be strongly dependent on the Co content (*7*). The effect of coadsorbed gases (*n*-hexane, oxygen) was also investigated.

EXPERIMENTAL

A series of monometallic and bimetallic catalysts with varying Pt/Co atomic ratios were prepared. All samples were prepared by the wet impregnation method. The precursors, H_2PtCl_6 and $CoCl_2$ (Soekawa Co.), were dissolved in water to which a small amount of concentrated hydrochloric acid was added (during the wet impregnation, all solutions contained the same amount of chlorine). Following the addition of the support (aerosil 200, Degussa), the water was evaporated at 373 K. Subsequently, the catalysts were dried in air for 16 h at 383 K. The monometallic Pt and the bimetallic Pt–Co catalysts contained 0.1 mmol metal/g catalyst. The (poorly dispersed) monometallic Co system contained 5 wt% (1.18 mmol metal/g catalyst) of Co.

For each (dried) sample, 40 mg was pressed (p = 30 kg/cm) into a disk with a

TABLE 1

Average Particle Sizes of the Aerosil-Supported Pt/Co Catalysts Obtained by Electron Microscopy

Pt/Co	*d* (nm)
100/0	5
90/10	5
80/20	5
50/50	4
20/80	3
0/100	200

diameter of 10 mm. The disk was placed in an infrared cell, equipped with NaCl windows, and reduced overnight by pure (flowing) hydrogen (p_{H_2} = 100 Torr (1.3 × 10^4 Pa)) at 720 K. Evacuation of the system resulted in a pressure of better then 10^{-6} Torr. The adsorption of CO on the freshly reduced/pretreated samples took place at 300 K. Usually, the spectra were recorded under two different conditions; at a relatively low pressure of CO ($p_{CO} < 10^{-6}$ Torr) and at a relatively high pressure of CO (p_{CO} = 50 Torr). The spectra were recorded in the 2200- to 1800-cm^{-1} region at 300 K. Each spectrum was obtained after collecting 256 scans. All experiments were performed using a FTIR JEOL JIR-10 (double beam) spectrophotometer.

RESULTS

The average particle sizes of the catalysts discussed below were determined by electron microscopy. The results are listed in Table 1.

First, the results of the freshly reduced samples will be given. Even small variations in the amount of CO adsorbed, caused by variations in the CO pressure, can result in appreciable variations in the position of the absorption band maximum, $\tilde{\nu}$(CO) on Co (*20*). Therefore, for all of the catalysts stud ied, two $\tilde{\nu}$(CO) values were determined. These corresponded to a relative "low" and a relative "high" pressure. The "low" pressure value for $\tilde{\nu}$(CO) was obtained by admitting CO to the sample at 0.5 Torr for 2 min followed by evacuation of the gas-phase CO ($p_{CO} < 10^{-6}$ Torr). The "high" pressure value was obtained at p_{CO} = 50 Torr after equilibration for 5 min. For Pt, the difference between the values obtained for the two pressures is small. (N.B. increasing the adsorption time of CO does not cause any differences in the results of the "low" and "high" pressure experiments.)

In Fig. 1 the IR absorption frequencies of CO (above 2000 cm^{-1}) adsorbed on the Pt–Co systems are shown as a function of the (bulk) Pt content. An absorption maximum was always present at about 1880 cm^{-1} (weak intensity and poorly resolved) due to the multicoordinated CO, but it will not be discussed further. The addition of Co to Pt causes a decrease in the frequency of adsorbed CO. This decrease is nearly linear and can be observed for both the low- and the high-pressure states. The high-pressure state wavenumbers are higher by about 10 cm^{-1} than those of the low-pressure states. When extrapolated to a zero Pt content in the catalyst, the experiments at the low-pressure state show a value of about 2040 cm^{-1}. This wavenumber has been reported (*21*) as the singleton frequency of CO adsorbed on Pt (the absorption maximum ob-

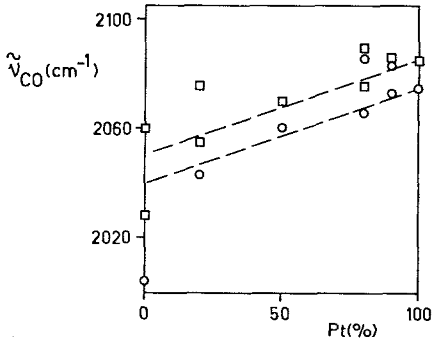

FIG. 1. The position (in cm^{-1}) of the absorption maximum $\tilde{\nu}$(CO) vs the Pt content in the sample for two pressures of CO; (○) $p_{CO} < 10^{-6}$ Torr, (□) p_{CO} = 50 Torr.

served for a surface coverage which approaches zero). The monometallic Co catalyst shows more drastic changes in the IR spectrum with the variation in the equilibrium pressure of CO (Fig. 2). When the CO pressure was increased, a blue shift in $\tilde{\nu}$(CO) was observed. A second absorption maximum, 2000 cm^{-1} ($p_{CO} < 10^{-6}$ Torr) → 2065 and 2028 cm^{-1} (p_{CO} = 50 Torr), was also observed. Mohana Rao *et al.* (*20*) observed a comparable shift with only one major maximum which appeared at 2050 cm^{-1} at a high CO pressure (p_{CO} = 40 Torr). Evacuation ($p < 10^{-3}$ Torr) at room temperature yielded a single maximum at 2015 cm^{-1}. The method of preparation of the catalyst might explain this difference: the wet impregnation of $CoCl_2$ vs the gas-phase sublimation of $Co_2(CO)_8$.

Two Pt-rich bimetallic samples upon CO adsorption (p_{CO} (equilibrium) $< 10^{-6}$ Torr) show spectra with two absorption maxima above 2000 cm^{-1}: the Pt/Co = 8/2 catalyst at 2086 and 2067 cm^{-1}, the Pt/Co = 9/1 catalyst at 2083 and 2072 cm^{-1}. These results deviate from the other Pt and Pt–Co systems studied here, as they all show only one absorption maximum above 2000 cm^{-1} (see Fig. 3). It is relevant to mention here that Toolenaar *et al.* (*15*) also observed three bands in the IR spectrum following the adsorption of CO on freshly reduced alumina-supported Pt; one band below 2000 cm^{-1} (due to the multicoordinated CO), the main band at 2073 cm^{-1}, and a satellite peak at 2080–2085 cm^{-1}. Daniel (*22*) obtained a similar spectrum upon the adsorption of CO on a cerium oxide-supported Pt (2 wt%) sample; the absorption maxima appeared at 2085, 2071, and below 1900 cm^{-1}. Palazov *et al.* (*4*) also distinguished three maxima at 2080, 2065, and 1852 cm^{-1}, respectively, on an alumina-supported Pt (0.5 wt%) catalyst. However, the monometallic aerosil-supported Pt studied in this paper revealed only one absorption maximum above 2000 cm^{-1} at 2075 cm^{-1}, as shown in Fig. 3. The double peak structure was only observed on the two Pt-rich Pt–Co samples.

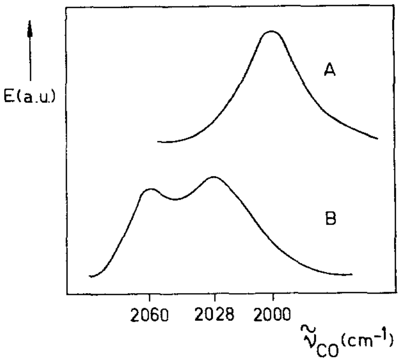

FIG. 2. The IR spectra of CO adsorbed on the monometallic Co system for two pressures of CO: (A) $p_{CO} < 10^{-6}$ Torr, (B) p_{CO} = 50 Torr. Extinction in arbitrary units, ambient temperature.

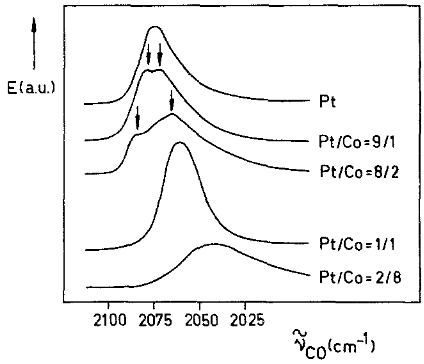

FIG. 3. The IR spectra of CO adsorbed on the Pt–Co samples ($p_{CO} < 10^{-6}$ Torr). Composition of the samples is indicated.

By means of a controlled desorption of CO, the effect of the surface coverage on the peak position was investigated. In these experiments the freshly reduced sample which was covered by CO (p_{CO} = 0.5 Torr, 2 min) at 300 K was heated and evacuated for 5 min at the desired temperature. This was followed by cooling to 300 K. At this temperature the spectrum was recorded. The sequence of heating, cooling, and scanning was repeated several times with an increasing desorption temperature (ΔT = 50 K) until almost no IR absorption could be observed. In Fig. 4 the position of the

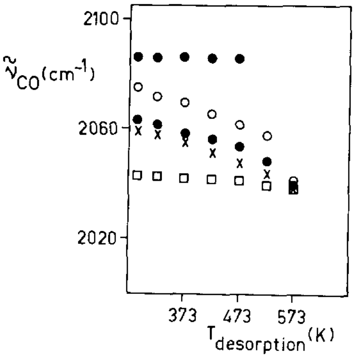

FIG. 4. The position of the absorption maximum, $\tilde{\nu}$(CO), for CO associated with Pt, as a function of the desorption temperature for various samples; (○) Pt, (●) Pt/Co = 8/2, (×) Pt/Co = 1/1, (□) Pt/Co = 2/8. Ambient temperature, $p_{CO} < 10^{-6}$ Torr.

absorption band maxima of several samples are shown as a function of the desorption temperature. Heating of the samples to a temperature in excess of 573 K resulted in the complete disappearance of the absorption maxima. The wavenumbers of the absorption maxima decrease with increasing desorption temperature to a value around 2040 cm^{-1}, irrespective of the composition of the catalyst. It can be observed that upon desorption the monometallic Pt system undergoes the largest red shift of 35 cm^{-1} (2075 → 2040 cm^{-1}). On the other hand, the Pt/Co = 2/8 system shows only a small decrease in wavenumber as a function of the desorption temperature: 2045 → 2038 cm^{-1}. These observations strongly suggest that the decrease caused by alloying Pt with Co is a result of a decrease in the CO dipole–dipole interaction (*21, 23*). The fact that the bimetallic systems (in particular the Pt/Co = 2/8 catalyst) show about the same singleton frequency as the monometallic Pt system suggests the absence of electronic structure effects. The IR absorption peak at 2086 cm^{-1} obtained for the Pt/Co = 8/2 system does not show a red shift when the desorption temperature is increased and the surface coverage of CO is decreased. This observation is shown in Fig. 5. This peak disappears at a desorption temperature (about 470 K) lower than that of the main peak at 2067 cm^{-1}. Only the main peak shows a red shift to a value of about 2040 cm^{-1}. The two poorly resolved absorption maxima of the Pt/Co = 9/1 system show a similar behavior; the position of the high-frequency peak (2082 cm^{-1}) is less affected by the desorption of CO. Daniel (*22*) also observed that the position of the high-frequency band remained approximately constant (2087 cm^{-1}) when the surface coverage of CO was decreased by evacuation at room temperature.

For the CO desorption experiments, the position of only one peak was affected. By isotopic dilution the position of both absorption maxima as seen with the Pt/Co = 8/2 system can be influenced as shown in Fig. 6. An increase in the ^{13}CO content in the mixture (by which dilution of the adsorbed ^{12}CO on the surface occurs) causes a red shift for both absorption maxima. A comparison of the desorption and dilution experiments might lead one to conclude that the position of the 2086-cm^{-1} peak is influenced by the clustering of adsorbed CO molecules.

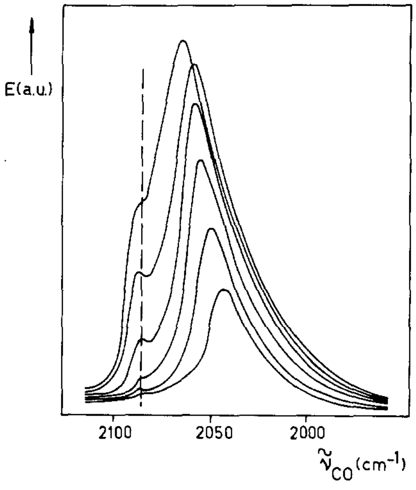

FIG. 5. The IR spectra recorded at ambient temperature of CO adsorbed on the Pt/Co = 8/2 system. The spectra are presented in the order of decreasing surface coverage. Partial desorption is achieved by short heating (300–573 K).

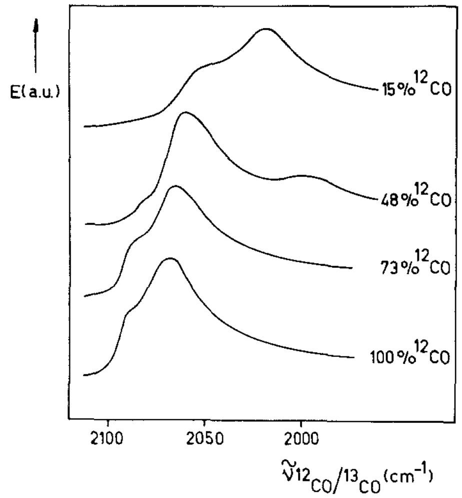

FIG. 6. The IR spectra of the $^{12}CO/^{13}CO$ mixtures adsorbed on the Pt/Co = 8/2 system. Content of ^{12}CO in the mixture is indicated; p_{CO} = 20 Torr, ambient temperature.

Island formation does not appear to be affected by repeated heating/cooling cycles.

As previously reported, coadsorption of CO on a surface with adsorbed oxygen causes a blue shift of the absorption band maximum of adsorbed CO (*15, 24*). In addition to the effect of oxygen on the band maximum of adsorbed CO, the effect of the oxidation state of the metal (Co) must be considered. Co oxide is more difficult to reduce and cobalt is also more easily oxidized in comparison to Pt. In this study the reduced Pt–Co samples have been subjected to a standard oxygen treatment (p_{O_2} = 0.5 Torr, T = 320 K, 5 min) before CO (p_{CO} = 0.5 Torr, T = 300 K, 2 min) was admitted to the IR cell. Following evacuation of the system blue shifts in the IR band maxima can be observed (shifts with regard to the results on samples which were not oxidized). These results are shown in Fig. 7. The blue shift increases with an increasing Co content in the catalysts ($10 \rightarrow 20$ cm^{-1}). In this respect it is noteworthy that due to the oxygen pretreatment, the absolute intensities differ considerably compared to the samples which had not been oxidized. With the Pt-rich samples there is very little change in the observed band intensity (partly because oxygen is removed by CO), whereas the Co-rich samples show a decrease in intensity as a result of oxygen pretreatment. The monometallic Co sample shows a weak absorption maximum at 2170 cm^{-1}, which can be attributed to CO adsorbed on oxidized Co. A peak at a similar position was not observed for any of the other samples. This is important for the earlier study (*7*) since it indicates the absence of unalloyed Co (and probably also of Co-rich surfaces) in the bimetallic systems. Reasonable mixing of both components at the surface is therefore most likely. Re-reduction of the oxidized samples (p_{H_2} = 100 Torr, T = 700 K, 30 min) resulted in the same spectra as those discussed in relation to Fig. 1.

At temperatures around 470 K, Co is known to be capable of dissociating CO easily (*25*), in contrast to Pt. The effect of alloying has been investigated in this study by passing CO (p_{CO} = 10 Torr) at 470 and 570 K over the sample. This was followed by evacuation and subsequent cooling to 300 K. Again, the spectra were recorded at a "low" and at a "high" pressure of CO ($p_{CO} < 10^{-6}$ Torr, p_{CO} = 50 Torr, resp.). As shown in Fig. 8, the CO treatment at 470/

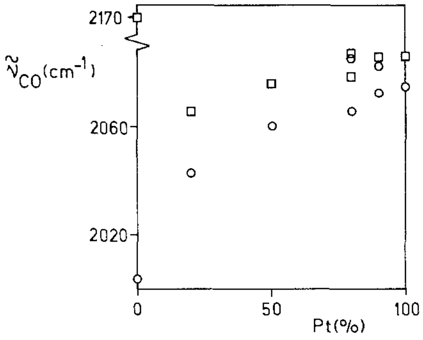

FIG. 7. The position of the absorption maximum, $\tilde{\nu}$(CO), vs the Pt content in the samples; (○) CO adsorbed on the freshly reduced sample; (□) CO adsorbed after the preadsorption of O_2 ($p_{CO} < 10^{-6}$ Torr, ambient temperature).

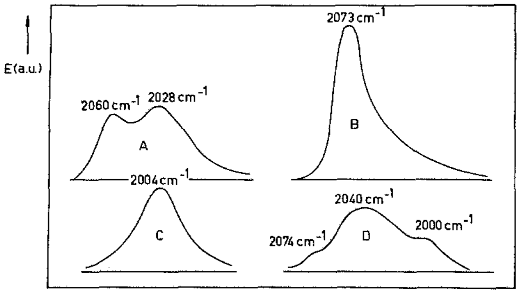

FIG. 8. The IR spectra recorded at ambient temperature of CO adsorbed on the monometallic Co system. (A) Freshly reduced (p_{CO} = 50 Torr); (B) pretreatment with CO at 473/573 K (p_{CO} = 50 Torr); (C) freshly reduced ($p_{CO} < 10^{-6}$ Torr); (D) pretreatment with CO at 473/573 K ($p_{CO} < 10^{-6}$ Torr).

570 K causes a substantial change in the IR spectra of CO adsorbed on Co. Fig. 8B shows a high-intensity absorption maximum at 2073 cm^{-1}. The spectrum as shown in Fig. 8A (CO adsorbed on freshly reduced Co) was obtained following reduction at 700 K (p_{H_2} = 100 Torr, 30 min). After evacuation for 1 h, spectra 8A and 8B were converted into 8C and 8D. The spectrum shown in Fig. 8D contains three absorption maxima. The peak at about 2000 cm^{-1} is comparable to that observed in Fig. 8C, and is aligned to CO adsorbed on metallic Co. The absorption maximum at 2073 cm^{-1} could appear as a result of the dissociation activity of Co but the formation of Co–carbonyl species should not be excluded. Literature data on IR spectra of Co–carbonyl structures such as $Co_2(CO)_8$ and $Co_4(CO)_{12}$ show absorption band maxima between 2070 and 2000 cm^{-1} (*26, 27*). In the IR spectra of $Co_2(CO)_8$, the peaks at about 2070, 2042, 2030, and 2022 cm^{-1} have a relatively high intensity. The spectra of $Co_4(CO)_{12}$ show strong absorption maxima at 2063 and 2055 cm^{-1}. This supports the theory that the peaks at 2060 and 2028 cm^{-1} (Fig. 8A) and 2040 cm^{-1} (Fig. 8D) might be the result of the formation of Co–carbonyl compounds. The dissociation of CO would then result in the formation of "C" (coke, carbide, or less likely graphite), adsorbed oxygen, and CO_2. The adsorbed oxygen could affect the frequency of adsorbed CO by oxidation of the Co surface. However, a band around 2170 cm^{-1} was not observed (CO adsorbed on oxidic Co^{n+}; see Fig. 7). It is worth mentioning here that the satellite peak in the spectra of the Pt-rich systems disappears by the CO treatment at high temperatures. However, the main IR maxima do not show shifts and/or changes in intensity. Probably, the surfaces corresponding to the satellite peak are covered by coke produced by the dissociation of CO (on Co). For all of the bimetallic systems, no change in the IR spectra due to the formation of Co–carbonyl species was observed.

We investigated the effect of coke/carbide formation on the absorption band maxima by using *n*-hexane to deposit a carbon-rich layer. The result of the *n*-hexane pretreatment on the absorption frequency of adsorbed CO is shown in Fig. 9. The site blocking at 473 and 573 K results in a red shift, the size of which depends on the Pt content of the sample. The Pt-rich samples show a relatively large shift due to coking compared to that of the Co-rich samples. The monometallic Pt system shows an IR shift of 20 cm^{-1} after blocking at 473 K and a shift of 26 cm^{-1} after blocking at 570 K. The *n*-hexane pretreatment of the Pt/Co = 2/8 sample results in a relatively small IR shift to 2040 and 2035 cm^{-1}, respectively.

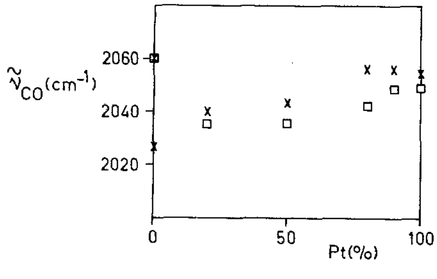

FIG. 9. The position of the IR absorption maximum upon CO adsorption at ambient temperature, $\tilde{\nu}$(CO), vs the Pt content in the sample after pretreatment with *n*-hexane ($p_{n\text{-hexane}}$ = 0.5 Torr) at (×) 473 K and (□) 573 K ($p_{CO} < 10^{-6}$ Torr).

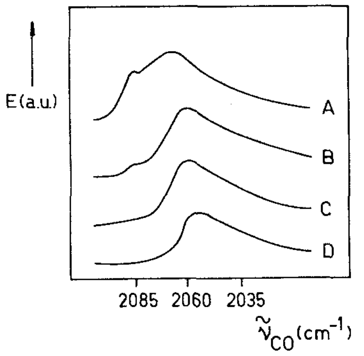

FIG. 10. The IR spectra recorded at ambient temperature of CO adsorbed on the bimetallic Pt/Co = 8/2 system. (A) Clean surface; (B–D) increasing exposure to *n*-hexane (10, 60, and 300 s; $p_{n\text{-hexane}} = 0.5$ Torr). $P_{CO} < 10^{-6}$ Torr.

This result can be explained by the fact that an additional dilution of the Pt ensembles (in the Co-rich systems), which are already small due to dilution by Co, has only a slight additional effect on the band frequency. The satellite peak in the Pt/Co = 8/2 system disappears rather quickly after blocking with *n*-hexane at 473 K, whereas the main peak retains a considerable intensity, as shown in Fig. 10. Coking of the monometallic Co system at 470–570 K results in a decrease in the intensity of the IR maximum at 2028 cm^{-1} and an increase in the peak at 2060 cm^{-1}. The same pretreatment of the monometallic Pt and of the bimetallic systems leads to a large red shift and a very strong decrease in the intensity of the IR absorption maxima. At a higher temperature (670 K) coking of the Co system still does not change the IR spectrum significantly whereas all the other systems, when coked at this relatively high temperature, show an absorption maximum around 2040 cm^{-1} with a very weak intensity. This is in agreement with the results obtained for hydrocarbon/hydrogen reactions. These experiments clearly show that the bimetallic systems are deactivated more severely while the monometallic Co catalyst actually became more active with time. This means that the catalytically active metal surface area of the monometallic Co system does not decrease during the *n*-hexane/hydrogen reactions.

DISCUSSION

The extent of reduction of a catalyst can play an important role with respect to the selectivity/activity of a catalyst (see for example Refs. (*28–30*)). Quantitative analyses of the reduction of the supported Co catalysts performed by various authors show large variations. A temperature-programmed reduction study by van 't Blik *et al.* (*31*) shows an almost complete reduction at 600 and 653 K of silica- and alumina-supported Co catalysts, respectively. Reuel and Bartholomew (*32*) found a 73% reduction of a silica-supported Co catalyst at 670 K. Our determination of the degree of reduction of the Pt–Co and Co catalysts (by the "sulfuric acid method" (*7*)) indicated that (a) Pt increases the extent of reduction of Co and (b) silica-supported systems are reduced to a much greater extent than the alumina-supported catalysts. The extent of reduction of silica-supported Co catalysts varies from 85 to 81%. In the studies mentioned above only an overall analysis is possible. However, the location of the ionic species (at the surface, at the metal–support interface, or in the bulk of the support) is of great importance and the presence of various forms of Co at the surface can be checked by IR spectroscopy. The absorption maxima of CO adsorbed on reduced and ionic Co differ considerably: 2000 cm^{-1} vs 2170 cm^{-1}. It is important to note that none of our freshly reduced mono- and bimetallic Pt/Co catalysts show an absorption maximum near 2170 cm^{-1}, irrespective of the pressure of CO (see Fig. 1). For this reason the conclusion can be made that although Co^{n+} is present on the catalysts (*7*), it is not accessible to CO. Neither is there any indication of unalloyed metallic Co in the Pt–Co catalysts. This is an important conclusion for the interpretation of the earlier data (*7*).

It is important to discriminate between the geometric (ensemble size) and electronic structure (ligand) effects which might be induced by Co and/or Co^{n+}. Zyade *et al.* (*10*) investigated the skeletal isomerization and hydrogenolysis of hexanes on alumina-supported Pt–Co catalysts. They explained the relation between the cyclic mechanism of isomerization and the reduction temperature of the catalyst mainly by the consideration of electronic factors. Therefore, experiments have been performed (see above) which should bring some information to bear on this point. In this study the effect of decreasing CO surface coverage was investigated on all samples. The monometallic Pt system shows a shift from 2075 cm^{-1} (at high surface coverage) to a value of about 2040 cm^{-1} (at a very low surface coverage). If there had been an electronic structure effect of alloying Pt with Co, this should have had an influence on the $\tilde{\nu}$(CO) in the whole range of θ(CO). At full CO surface coverage, a decrease in the frequency of the absorption maximum from 2075 to 2040 cm^{-1} is observed with increasing Co content. On the other hand, a decrease in the surface coverage by means of a controlled desorption of CO had only a small influence on the peak position of the Co-rich (Pt/Co = 2/8) sample. At very low surface coverage, a value of about 2040 cm^{-1} was obtained for $\tilde{\nu}$(CO). Apparently, a decrease in the CO surface coverage on pure Pt and alloying with Co both have the same effect on the position of the absorption maximum. This result strongly suggests that the red shift observed (only) at high θ(CO) on Pt is due to the dilution of Pt by Co. No additional (red) shift has been observed due to the potential electronic effect of Co or due to the Co^{n+} coming into contact with the Co at the surface.

Addition of a relatively small amount of Co to Pt results in the appearance of a second absorption maximum in the 2086 to 2083-cm^{-1} region. The monometallic Pt and the Co-rich systems do not show absorptions in this region. However, a peak at a similar position was observed on different supports (*4, 15, 22*). Surface blocking by the adsorption of *n*-hexane at 470 K as described in this paper results in the rapid disappearance of the peak at 2086 cm^{-1} in comparison with the behavior of the IR maximum at the lower wavenumber. This last peak shifted under these (mild) conditions from 2067 to 2056 cm^{-1} and retained a rather high intensity. Toolenaar *et al.* (*15*) observed comparable behavior following pretreatment by ethylene on alumina-supported Pt. It should be mentioned here that the deactivation by hydrocarbons strongly depends on the surface roughness of the catalyst, relatively smooth surfaces being blocked more easily. Lankhorst *et al.* (*33*) found that catalysts having a high dispersion (with a high number of edge and corner atoms) are much more resistant to deactivation than catalysts with a low dispersion (many close-packed crystal surfaces). Somorjai and Blakely (*34*) stated that the relatively high rate of dissociation of hydrogen on steps and kinks may keep these sites active. Obviously, hydrocarbons can easily suppress or even eliminate CO adsorption on these smooth surfaces. For this reason, we suggest that the absorption maximum at the higher wavenumber (2086/2083 cm^{-1}) is probably caused by CO adsorbed on smooth regions of the surfaces. However, the only safe conclusion is that two different sites are open to CO on the surfaces of the bimetallic catalysts. Addition of Co to aerosil-supported Pt, just like using alumina or ceriumoxide as a support, induces the formation of smooth surfaces which are otherwise absent on Pt/aerosil. Island formation of CO (on smooth surfaces) would then explain the constant position of the high-frequency band when the surface coverage is decreased. Altman and Gorte observed two desorption states of CO at 400 and 510 K on alumina-supported Pt (*35*). The relative intensity of the peak at 400 K increased with increasing particle size. This low-temperature state has been ascribed to CO desorbing from (111)-type terraces on the larger particles; the desorption maximum for saturation coverage on Pt (111) is approximately 400 K (*36*). As can be seen in Fig. 5, the IR maximum at 2086 cm^{-1} compared to the main absorption maximum disappears at a lower desorption temperature. This also supplies evidence for the "smoothness" of the planes related to the IR maximum at 2086 cm^{-1}. Infrared studies (*23, 37*) of CO adsorbed on the Pt (111) single-crystal surface show bands around 2100 cm^{-1} at full surface coverage. This relatively high wavenumber also supports the idea that the IR maximum at 2086 cm^{-1} is due to the adsorption on smooth surfaces.

Blocking of the surface by *n*-hexane prior to CO adsorption results in a strong red shift and a decrease in the band intensity for all Pt and Pt–Co samples. Several authors explain this effect by invoking electronic effects of coadsorption with electron-donating molecules such as ethylene and benzene (*38, 39*). This study, however, does not show an additional decrease in the $\tilde{\nu}$(CO) wavenumber due to any kind of electronic interaction between the metal and the carbon-containing layer. Coking of the samples at 573 and 673 K results in absorption maxima of CO at values around 2040 cm^{-1}, a value which can be explained by pure dilution effects of the deposits. Coking of the Co catalyst neither affects the activity (in hydrocarbon reactions) nor the adsorption of CO very much, as is shown in this study. The fragments C_yH_x are probably continuously and easily removed from the Co surface. Probably continuous cleaning of the metal surface is blocked by the addition of Pt to Co; on the bimetallic catalysts no such behavior due to the presence of unalloyed Co has been observed. The addition of only 20% Pt and Co causes a deactivation which is even more significant than that on pure Pt. However, hydrocarbon reactions with the Pt/Co = 2/8 system still show an almost Co-like character (*7*), i.e., a high preference for hydrogenolysis. The same has been observed with the Pt/Ir (*8*) and the Pt/Re (*9*) bimetallic catalysts. In contrast to Co, the pure Ir and Re catalysts do deactivate during hydrocarbon reactions, albeit slowly. Probably, the rate of C_yH_x removal on Co is faster than the further deactivation (e.g., conversion into graphite) of these species, while this removal on Ir and Re is slower.

CONCLUSIONS

(1) The shift in the absorption band frequency of CO adsorbed on Pt, caused by alloying of Pt with Co, is mainly due to the "dilution effect"; no evidence for the existence of an electronic structure effect has been found.

(2) The addition of a relatively small amount of Co to Pt results in the appearance of an absorption maximum at a relatively high wavenumber ($\tilde{\nu}$(CO)). This maximum can be ascribed to the adsorption of CO on smooth surfaces; this absorption maximum disappears quickly upon coking by *n*-hexane.

(3) The surface of Co is much more difficult to cover by carbonaceous deposits than that of the bimetallic surfaces. However, the addition of a relatively small amount of Pt to Co results in site blocking of the surface by *n*-hexane which also occurs in the case of pure Pt samples.

(4) Passing CO at elevated temperatures over Co results in the formation of Co–carbonyl species. Their formation is suppressed by the addition of Pt.

(5) Co^{n+}, which is known to be present in the bimetallic Pt–Co and monometallic Co systems, is not accessible to CO and thus not present at the surface.

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