FTIR study of the oxidation reaction of CO with O_2 over bimetallic Pd–Rh/SiO_2 catalysts in an oxidized state

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CO species adsorbed on the surface of oxidized bimetallic Rh–Pd catalysts, prepared by coimpregnation and sequential impregnation methods, were analyzed *in situ* by IR spectroscopy, during the reaction of CO with O_2 in an oxidizing atmosphere. The results show that the two methods of impregnation lead to the existence of oxidized Rh on the surface of the bimetallic catalyst, however, in the case of the sequential impregnation method, the Pd surface is more reduced than in the case of catalysts prepared by coimpregnation. The simultaneous presence of reduced Pd and oxidized Rh that occurs in the catalysts prepared by sequential impregnation allows the existence of a synergistic effect similar to that proposed in the literature for the Pt–Rh system. The lower degree of oxidation of the Pd in the catalysts prepared by sequential impregnation, is mainly due to the fact that the Pd in these catalysts comes from the organic precursor palladium acetylacetonate, while in the catalysts prepared by coimpregnation, the Pd comes from the precursor $PdCl_2$.

Keywords: CO oxidation, Rh–Pd, silica, synergism, catalysis

1. Introduction

The three-way catalysts currently used in motor vehicles for the elimination of CO, NO_x and hydrocarbon pollutants, are made by a combination of the noble metals Pt (Pd) and Rh. The presence of two or more metals may lead to the appearance of synergistic effects, i.e., that the joint activity of the metals may be greater than the sum of their separate activities. The presence of synergism was reported by Oh and Carpenter [1] in the case of Pt–Rh bimetallic catalysts prepared by the method of sequential impregnation, and it is absent if the catalyst is prepared by coimpregnation of both metals. According to Oh and Carpenter, the method of sequential impregnation leads to the formation of Rh clusters next to Pt clusters, giving rise to an interface between both metals. The synergistic effect would be caused by reaction at the Pt–Rh interface between the CO adsorbed on the reduced Pt and the oxygen on the surface of a neighboring Rh atom in an oxidized state. Later, Lakis et al. [2,3] found that there is also a synergistic effect with catalysts prepared by sequential impregnation in the reduction reaction of NO with CO and in the hydrogenation of NO with H_2. Similarly to the experimental evidence observed by Oh and Carpenter, the synergistic effect did not occur if the catalysts were prepared by coimpregnation.

In contrast with the Pt–Rh system, which has been the subject of several studies, little research has been done on the Pd–Rh system. The effect of the addition of Pt and Pd to supported Rh catalysts was studied by Schlatter and Taylor [4], who found that those metals increase the oxidizing activity, but have an undesirable effect on the NO_x reduction reaction, favoring the formation of NH_3 under reducing conditions. The surface enrichment of Pd–Rh films was studied by Moss and Gibbens [5], who concluded that a high Rh content led to a surface enrichment with Pd, decreasing the activity of the alloy. Del Angel et al. [6] studied the activity of bimetallic Pd–Rh catalysts prepared by coimpregnation in conversion reactions of methylcyclopentane and in the hydrogenation of benzene. The study confirms that the surface of supported bimetallic catalysts is very similar to that observed with the films of Moss and Gibbens, indicating that the coimpregnation method leads to the formation of alloys between both metals.

A series of studies have been carried out by the authors related to the activity of bimetallic Pd–Rh/SiO_2 catalysts in the reduced state, prepared by coimpregnation and sequential impregnation, in the oxidation reaction of CO with O_2 [7] and in the reduction of NO with CO [8]. Both studies showed that the catalyst prepared by sequential impregnation was always more active than the catalyst prepared by coimpregnation. However, the activity of the bimetallic catalysts prepared by sequential impregnation was less than the sum of the activities of the monometallic catalysts, and there was no evidence of a synergistic effect. In contrast, if the catalysts were previously calcined at 500 °C and the oxidation reaction of CO with O_2 was carried out under oxidizing conditions (30% O_2 and 5% CO), a strong synergistic effect was observed with the catalysts prepared by sequential impregnation, within the temperature range of 100 °C and the catalyst's ignition temperature [9]. The bimetallic catalysts prepared by coimpregnation did not show a synergistic effect under the above reaction conditions. The synergistic effect decreased considerably if the catalyst was subjected to a treatment that increased the degree of reduction of the metals on the surface, in agreement with the lack of a synergistic effect seen with those bimetallic catalysts in a reduced state [7].

The fact that the synergistic effect decreased when the surface metals underwent reduction, allows the assumption that the synergistic effect observed with our bimetallic Pd–Rh/SiO_2 catalysts prepared by sequential impregnation, could be explained by a mechanism similar to the one proposed by Oh and Carpenter for their Pt–Rh catalysts prepared also by sequential impregnation. If Pd and Rh are reduced, the CO is adsorbed on the surface of both metals and consequently the synergistic mechanism cannot occur since the only reaction pathway is through the adsorption of O_2 on the catalyst's surface.

The purpose of the present work was to establish whether, under the reaction conditions that lead to the synergistic effect of our Pd–Rh catalysts, the basic conditions for the mechanism proposed by Oh and Carpenter to occur are fulfilled, i.e., the existence of CO adsorbed on reduced Pd, while the Rh surface is in the oxidized state. Therefore, the CO species adsorbed on the surface of the monometallic and bimetallic catalysts under the reaction conditions, described in our previous paper [9], were analyzed by IR spectroscopy. This is the most adequate technique for that purpose because it allows information to be obtained during the reaction on the oxidation state of the surface of both metals from an analysis of the IR bands of the CO molecules adsorbed on each of them.

2. Experimental

The monometallic and bimetallic catalysts containing 2% total metal charge, and composed of 100% Rh (100Rh), 70% Rh and 30% Pd (70Rh–30Pd), 33% Rh and 67% Pd (33Rh–67Pd), and 100% Pd (100Pd), prepared by the methods of coimpregnation (CI) and sequential impregnation (SI), are the same that were used in our previous work [9]. In brief, the monometallic and bimetallic catalysts were prepared with 2% total metal charge on Cabosil 5H. In the CI method, the appropriate quantities of the inorganic salts $RhCl_3$ and $PdCl_2$ are dissolved and the metallic support is impregnated by the wetness impregnation method. In the SI method, in a first step the $RhCl_3$ is impregnated, followed by calcination at 500 °C, and in a second step the support is impregnated with a solution of Pd acetylacetonate in dichloromethane to avoid dissolving the Rh impregnated in the previous step. The monometallic catalysts were prepared by the wetness impregnation method with the corresponding $PdCl_2$ or $RhCl_3$ inorganic salt.

The catalysts impregnated as described were calcined at 500 °C for 3 h under a pure oxygen flow of 10 cm^3/min. Then, without prior reduction, the catalyst discs were prepared for insertion in the IR reactor cell (ISRI Research & Development, Indiana, USA). The reactor cell is provided with gas inlet and outlet and temperature control, and has CaF_2 windows that allow the *in situ* analysis of the CO species adsorbed on the catalyst's surface under the desired reaction conditions. The catalyst discs were made in a hydraulic press under a pressure of 13 000 psi.

The disc in the reactor cell was placed in the IR spectrophotometer chamber, and a mixture of 30% (v/v) O_2 in helium was allowed to flow at approximately 100 cm^3/min. The reactor cell temperature was increased to 135 °C and kept constant for 35 min to eliminate the water adsorbed on the support, and a background spectrum of the sample was made. The reactor cell was then cooled to room temperature and CO was allowed to flow until a CO concentration of 5% (v/v) was reached in the gas phase. The temperature of the reactor cell was then increased to 135 °C with the CO, H_2 and helium mixture flowing through. When the temperature of 135 °C was reached, the IR spectrum of the sample was taken using the background spectrum obtained previously. In this way the IR spectrum will show only the signals corresponding to CO in the gas phase and the CO species adsorbed on the catalyst's surface. The heating rate of the reactor cell was the same as that used in the kinetics experiments reported in our previous paper [9], in order to reproduce as closely as possible the conditions used in that work.

An IR spectrum of CO in the gas phase was also obtained using a silica disc without catalyst, adjusting the temperature and the flow of reagents and helium through the reactor cell to the same conditions described previously. This gas-phase spectrum of CO will be used later to eliminate the overlap of the gaseous CO band and the bands of CO adsorbed on the surface of the oxidized catalysts. The IR spectra were made on a Bruker model Vector 22 instrument at a resolution of 2 cm^{-1} and with 20 scans per spectrum.

In addition to the catalysts prepared previously [9], two new catalysts have now been prepared. One of them is a monometallic catalyst having 2% Pd on silica, prepared by impregnation of the support with the organic salt acetylacetonate, using dichloromethane as the solvent. This catalyst will be designated 100Pd-ORG. The second is a bimetallic catalyst with a 2% total load composed of 70% Rh and 30% Pd, prepared by coimpregnation of the organic salts palladium acetylacetonate and rhodium-dicarbonyl acetylacetonate, dissolved in dichloromethane. This new bimetallic catalyst will be designated 70Rh–30Pd CI-ORG. Both catalysts were calcined in the same way as the other catalysts, and were subjected to experiments for determining their activity, and to FTIR analysis of the species adsorbed on the surface during the reaction. The determination of the activity was made as described previously [9], using a piston flow reactor operating under differential conditions. Similarly to the catalysts in our previous work, in order to express the activity as TON, part of the calcined catalysts was reduced with a mixture of 5% H_2/Ar at 300 °C for 1 h, and their dispersion was determined by chemisorption of H_2 at 60 °C. The dispersions were found to be 37.2% for 100Pd-ORG and 42.1% for 70Rh–30Pd CI-ORG. It is clear that the number of metal atoms on the surface of the oxidized catalysts can be different from that found by chemisorption in the reduced state, but because the reduction is carried out under moderate temperature conditions, it is reasonable to assume that the difference should not be large. In any case, not considering the dispersion of the catalysts when comparing their activities may lead to important errors in the interpretation of the kinetics results.

3. Results and discussion

As already mentioned, in order to compare the results of this work with the kinetic data reported in our previous paper [9], the IR spectra of all the catalysts were obtained under the same reagent and inert flow conditions, i.e., a total flow of 100 cm^3/min, balanced with He, and 5% CO and 30% O_2 concentrations. Therefore, the state of the metals on the catalyst surface as well as the CO species adsorbed on it should be similar to those found in the previous kinetic studies. The temperature of 135 °C was chosen because it allowed the synergistic effect of the catalysts prepared by the sequential impregnation method to be seen clearly. The activity data at 135 °C for the different monometallic and bimetallic catalysts obtained in that work [9] are shown in table 1.

Figure 1(a) shows the IR spectrum obtained with the monometallic Rh catalyst (100Rh) after the reactor cell had reached a temperature of 135 °C while the CO, O_2 and helium reagent mixture was flowing through. Peaks at 2092 and 2032 cm^{-1} and a small shoulder at 2131 cm^{-1} are clearly seen. The 2092 and 2032 cm^{-1} bands have been observed by various researchers in the spectra of reduced Rh catalysts, and they are attributed to the adsorption of CO in the gem form on isolated Rh atoms on the surface of the support [10,11]. The oxidation state of Rh in those isolated atoms is believed to be 1+, among other reasons because of the experimental evidence obtained by oxidation of Rh clusters [12]. In fact, Kiss and Gonzalez [13] have shown that the oxidation of a Rh/SiO_2 catalyst for 1 h at a temperature of 300 °C, leads to an evident increase in the bands corresponding to the adsorption of CO in the gem form, and to the appearance of a band at 2103 cm^{-1} associated with the adsorption of CO on RH with an oxidation state greater than 1+. In the spectra of figure 1(a) a small shoulder at 2103 cm^{-1} can be seen, but much more evident is the appearance of a band at 2131 cm^{-1}, which may be due to the adsorption of CO on Rh with a higher oxidation state than that obtained by Kiss and Gonzalez, since in the present work the catalyst was oxidized for 3 h at 500 °C. On the other hand, none of the bands that may be attributed to the adsorption of CO on reduced Rh (linear or bridged) could be observed in the spectrum of this catalyst, so it can

Table 1
Activity of monometallic and bimetallic catalysts.[a]

Catalyst	TON × 10^4(mol CO_2/mol metal)
100Rh	9.1
100Pd	4.7
70Rh–30Pd CI	5.7
70Rh–30Pd SI	160.8
33Rh–67Pd CI	5.9
33Rh–67Pd SI	56.0

[a] Reaction conditions: at 130 °C, CO 1.5% (v/v), O_2 7.5% (v/v), total flow rate 100 cm^3/min, balanced with He (from [9]).

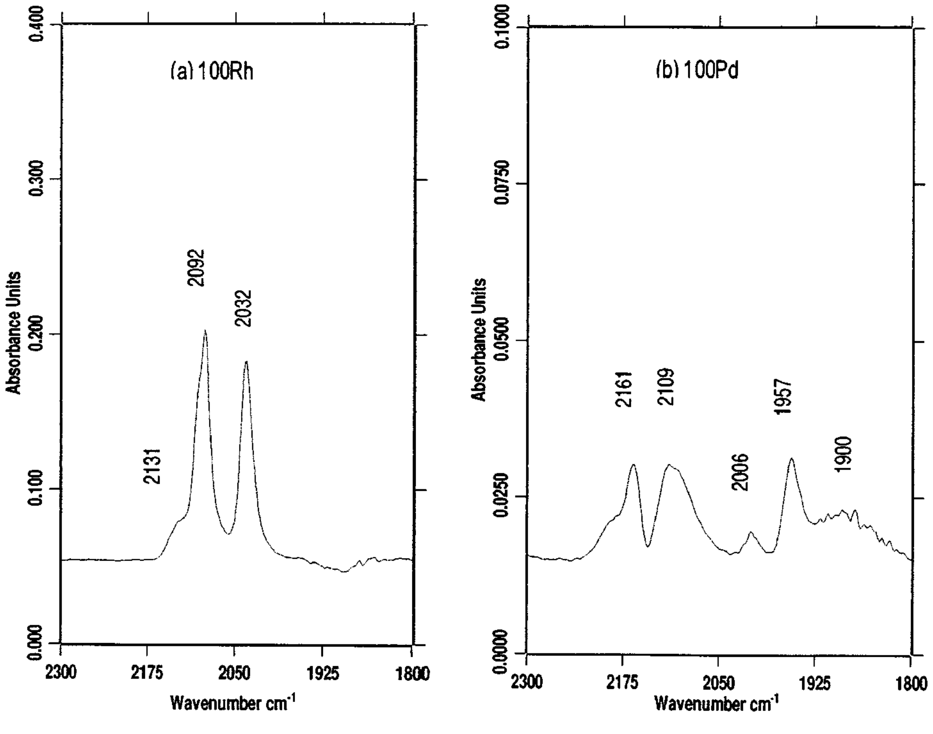

Figure 1. (a) IR spectrum of catalyst 100Rh at 135 °C, with a flow rate of 100 cm^3/min of a 5% CO, 30% O_2 mixture balanced with He; (b) the same as (a) but on catalyst 100Pd.

be concluded that the surface of the monometallic Rh is essentially oxidized.

Figure 1(b) shows the IR spectrum of CO adsorbed on the monometallic Pd catalyst (Pd100). A series of low intensity peaks can be seen clearly at 2161, 2109 and 2006 cm^{-1}, and a broad peak with maxima at 1957 and 1900 cm^{-1}. The interpretation of the IR spectrum shown in this figure and its relation with the oxidation state of Pd is somewhat more complicated than in the case of the Rh monometallic catalyst. Palazov et al. [14] carried out IR studies of the adsorption of CO on a 9% Pd/SiO_2 catalyst in the reduced and in the oxidized state. These authors found that at low CO coverage the IR spectrum of CO adsorbed on reduced Pd shows a broad non-Gaussian peak with a maximum at 1970 cm^{-1} and a shoulder at 1900 cm^{-1}, and a second smaller and sharper peak with a maximum at about 2070 cm^{-1}. As the CO coverage increased, a new peak with a maximum at 2095 cm^{-1} appeared which increased in intensity as CO coverage increased, making the 2070 cm^{-1} peak appear as a shoulder of the 2095 cm^{-1} peak at a CO coverage close to saturation. The 1900 and 1970 cm^{-1} bands were assigned by Palazov et al. to the adsorption of CO in bridge form, and the 2070 cm^{-1} band to the adsorption of CO in linear form. These authors found that if the catalyst was subjected to an oxidizing treatment at temperatures higher than 180 °C, important changes were produced in the IR spectrum of the adsorbed CO. In fact, the IR spectrum of CO adsorbed at room temperature on the Pd/SiO_2 catalyst, previously oxidized at a temperature of 300 °C for 5–10 min, showed a small broad peak with a maximum at about 1900 cm^{-1}, a second peak of greater intensity and non-Gaussian shape with a maximum at about 2103 cm^{-1}, and a small shoulder with a maximum at 2135 cm^{-1}. According to Palazov et al., the 1900 cm^{-1} peak would be associated with the adsorption of CO in bridged form, while the 2103 and 2135 cm^{-1} bands would be related to the adsorption of CO in linear form. If the oxidation temperature was increased to 450 °C, Palazov et al. found that the 1900 cm^{-1} almost disappeared, and only the 2103 and 2135 cm^{-1} bands can be seen. Therefore, the decrease in the intensity of the 1900 cm^{-1} band and the appearance of bands above 2100 cm^{-1} was a clear indication of a greater degree of oxidation of Pd.

The IR spectrum of the adsorption of CO on Pd, shown in figure 1(b), shows absorption bands at 1900 and 1957 cm^{-1}, which correspond to the adsorption of bridged CO. The low intensity of those bands, together with the appearance of the 2109 cm^{-1} band, which may be associated with the 2103 cm^{-1} band found by Palazov et al., are indications that the catalyst is essentially oxidized. The 2135 cm^{-1} band found by Palazov et al. is not seen in the spectrum of figure 1(b); there is, however, an IR band at 2163 cm^{-1}, which should correspond to CO adsorbed on Pd with a higher degree of oxidation than that of the catalyst of Palazov et al. This is reasonable, considering that the oxidation of our catalyst took place at 500 °C for 3 h, while Palazov et al.'s catalyst was oxidized at 450 °C for 5–10 min.

Figure 2(a) shows the IR spectrum of the bimetallic catalyst containing 70% Rh and 30% Pd prepared by the coimpregnation method (70Rh–30Pd CI). The spectrum shows two intense bands at 2097 and 2035 cm^{-1}. Moreover, there is a well defined shoulder at 2135 cm^{-1}, and there is a low intensity peak at 1957 cm^{-1}, even though the absorbance scale used does not allow it to be seen directly. The 2097

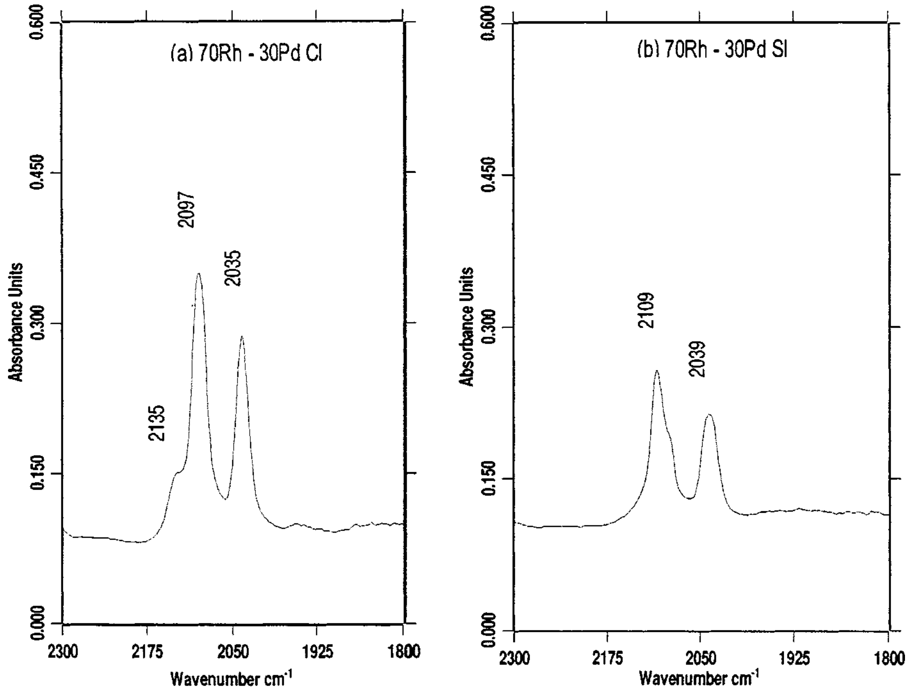

Figure 2. (a) IR spectrum on catalyst 70Rh–30Pd prepared by coimpregnation under the same conditions of temperature and reactant concentration as in figure 1; (b) the same as (a) but on catalyst 70Rh–30Pd prepared by sequential impregnation.

and 2035 cm^{-1} peaks may be associated with the adsorption of CO in the gem form, although the 2097 cm^{-1} peak is displaced to a higher frequency with respect to that of monometallic Rh, probably due to superposition of bands with other adsorbed CO species. The well defined peak at 2135 cm^{-1} is also seen with the monometallic Rh catalyst, and it has been reported by Pazalov et al. for the oxidized Pd catalyst, so that in principle it may be due to any of the metals in the oxidized state. The small peak at 1957 cm^{-1} corresponds to the absorption of CO on Pd, since it also appears in the spectra of the monometallic Pd catalyst.

The IR spectrum obtained using the catalyst having the same composition as above but prepared by the sequential impregnation method (70Rh–30Pd SI) catalyst is shown in figure 2(b). For this catalyst, the IR spectrum is dominated by two intense bands of adsorbed CO at 2109 and 2039 cm^{-1} which are probably generated mainly by the adsorption of gem-CO on Rh, although it is quite possible that there may be superposition of peaks of CO adsorbed on Rh and on Pd in the band seen at 2109 cm^{-1}. There is also a barely perceptible peak at 1950 cm^{-1} which may be assigned to the adsorption of bridged CO on Pd. The most noticeable difference with the catalyst prepared by coimpregnation is the complete absence of the peak at 2135 cm^{-1}, showing clearly that the Rh and/or Pd on the surface of the SI catalyst are less oxidized than on the surface of the catalyst prepared by coimpregnation.

The fact that the sequential impregnation method generates a bimetallic catalyst with a lower degree of oxidation than that obtained by the coimpregnation method is confirmed by the IR spectra shown in figure 3 (a) and (b) for catalysts 33Rh–67Pd CI and 33Rh–67Pd SI, respectively. The IR spectrum of the catalyst prepared by coimpregnation, figure 3(a), shows the gem-CO bands on Rh at 2094 and 2030 cm^{-1}, and a band at 2130 cm^{-1}. The latter band must belong to the adsorption of CO on oxidized Pd and/or Rh. The intensity relation of the 2130 cm^{-1} with respect to those corresponding to gem-CO is greater than that found for the 70Rh–30Pd CI catalyst with a higher Rh content. This suggests that the origin of that band may be associated mainly with the adsorption of CO on oxidized Pd, although it is not possible to discard that one part of it originates from the adsorption of CO on oxidized Rh. The band centered at around 1920 cm^{-1}, corresponding to the adsorption of CO on Pd, is also seen. In the IR spectrum of the catalyst prepared by sequential impregnation, shown in figure 3(b), it is only possible to see the bands corresponding to the adsorption of gem-CO on Rh at 2092 and 2032 cm^{-1}, and a small shoulder at 2103 cm^{-1}. Once again, no IR band is seen in the region of 2130 cm^{-1}, confirming that the catalyst prepared by sequential impregnation is in a lower oxidation state than the one prepared by coimpregnation.

Among the possible reasons for the SI bimetallic catalysts to be less oxidized than those prepared by coimpregnation is the fact that the precursors used to impregnate the Pd are different. In the case of the CI catalysts the inorganic salt $PdCl_2$ is used, while for the SI catalysts the Pd comes from the organic salt Pd acetylacetonate. It is known that different precursors can generate compounds on the surface of the support with a greater or smaller degree of difficulty for reduction, as has been reported, for example, by Worley et al. [15] for the case of Rh/Al_2O_3 catalysts prepared from different precursors. On the other hand, Lomot et al. [16]

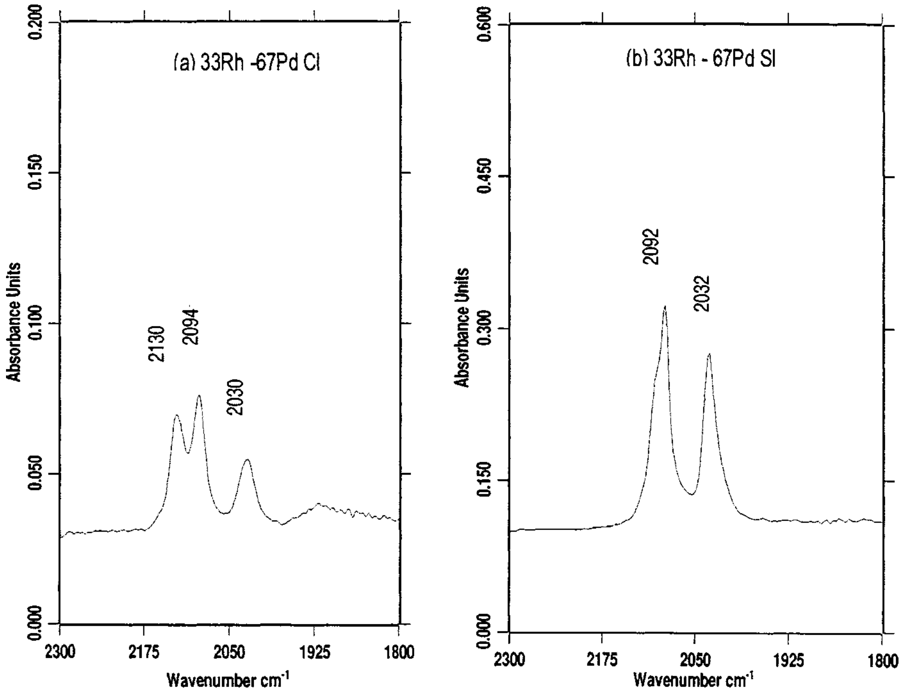

Figure 3. (a) IR spectrum on catalyst 33Rh–67Pd prepared by coimpregnation under the same conditions of temperature and reactant concentration as in figure 1; (b) the same as (a) but on catalyst 33Rh–67Pd prepared by sequential impregnation.

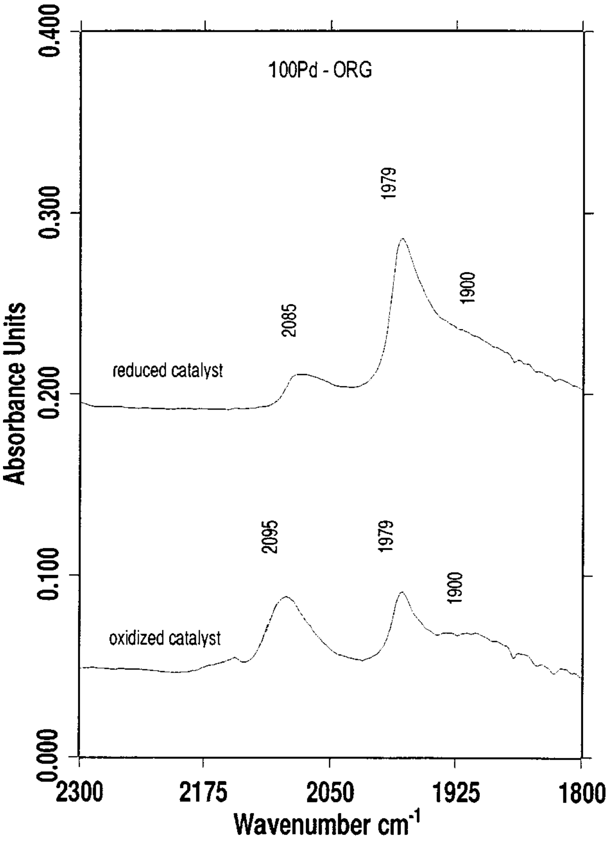

Figure 4. IR spectra of catalyst 100Pd-ORG prepared from the organic precursor palladium acetylacetonate, oxidized (calcined at 500 °C under O_2) and prereduced at 300 °C for 2 h with hydrogen. The same conditions of temperature and reactant concentration as in figure 1.

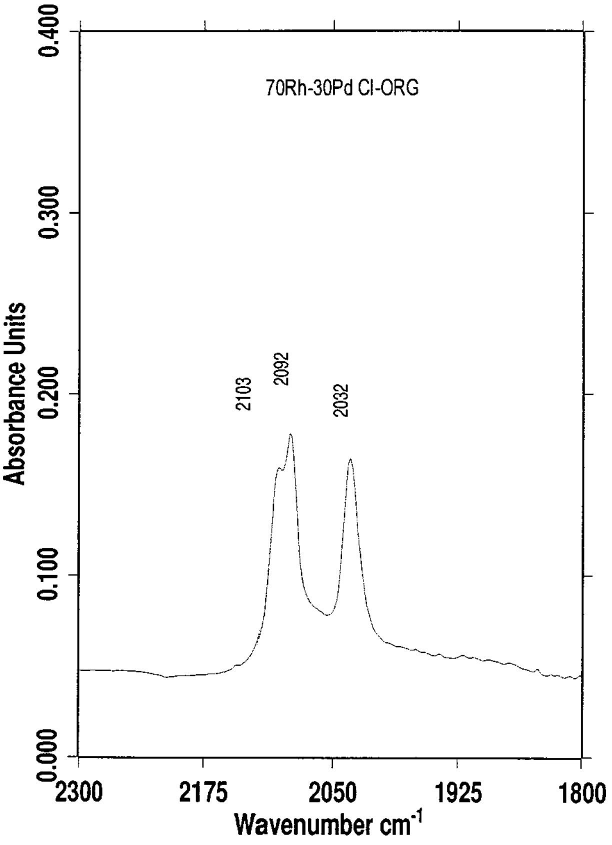

Figure 5. IR spectrum of catalyst 70Rh–30Pd CI-ORG prepared by coimpregnation of the organic precursors rhodium-dicarbonyl acetylacetonate and palladium acetylacetonate, under the same conditions of temperature and reactant concentration as in figure 1.

found that the activity of Pd/SiO_2 catalysts in the reactions of 2,2-dimethylpropane and n-hexane with H_2 can be strongly influenced by the pretreatment and the type of precursor used. Therefore, a monometallic catalyst with 2% Pd (100Pd-ORG) was prepared from palladium acetylacetonate. After impregnation, the catalyst was subjected to the same calcination process as the other catalysts, and the IR spectrum was obtained under the same conditions described above. This IR spectrum is shown in figure 4. Surprisingly, peaks are seen at 2095 and 1979 cm^{-1}, and a broad band at about 1900 cm^{-1}. Only a small band is seen in the region of oxidized Pd centered at 2143 cm^{-1}. The positions and the shapes of the peaks at frequencies below 2100 cm^{-1} are very similar to those found by Palazov et al. [14] in the case of the reduced Pd catalyst. Figure 4 also includes the spectrum of the 2% Pd catalyst previously reduced at 300 °C for 2 h in a mixture of 5% H_2 and argon. It can be seen that basically the same bands appear as with the calcined catalyst, only with greater intensity. The above shows that in the monometallic Pd catalyst prepared from the organic salt the surface of the Pd during the reaction is largely in the reduced state. Thus the reason for the lower degree of oxidation shown by the IR spectra of the SI catalysts as compared to the CI catalysts may be explained by the lower degree of oxidation of Pd in the former when they are prepared from the organic Pd salt.

Although it is known that the activity of reduced Pd is higher than in the oxidized state, the high activity of the SI catalysts cannot be explained on the basis of the higher activity of the reduced Pd present in the bimetallic SI catalyst. In fact, the activity of the Pd catalyst prepared from the organic salt and calcined at 500 °C, is 14.2×10^{-4} s^{-1} at 135 °C. This activity is greater than that obtained for the catalyst prepared from $PdCl_2$, which is shown in table 1, but is still far less than that of the bimetallic catalysts prepared by sequential impregnation. Clearly, the synergistic effect appears only if reduced Pd and oxidized Rh exist simultaneously on the catalyst's surface, generating the necessary conditions for the occurrence of the synergistic effect proposed by Oh and Carpenter [1].

As has been established in this work, the use of the inorganic salt $PdCl_2$ in the catalysts prepared by coimpregnation leads to an essentially oxidized Pd surface after the calcination process. The above prevents the existence of the synergistic effect seen with the catalysts prepared by sequential impregnation, where the use of the organic Pd salt as the precursor leads to a more highly reduced Pd surface. Therefore, it seems reasonable to assume that if the coimpregnated catalysts are prepared using the organic Pd salt, the synergistic effect may also occur. To check this point, the 70Rh–30Pd CI-ORG was prepared by coimpregnation with the organic salts rhodium-dicarbonyl acetylacetonate and palladium acetylacetonate dissolved in dichloromethane. The IR spectrum of this catalyst during the reaction at 135 °C is shown in figure 5. As can be seen, it is very similar to that of the catalyst prepared by sequential impregnation shown in figure 2(b). The gem CO bands are seen at 2032 and 2092 cm^{-1}, and there is a shoulder at 2103 cm^{-1} which has been attributed to the adsorption of CO on Rh with an oxidation state of 2+ or 3+. The activity of this catalyst at 135 °C was determined under the same conditions shown for the other catalysts, and a TON value of 180.4 s^{-1} was obtained. This activity value is even greater than that observed for the catalyst prepared by sequential impregnation, and shows clearly that the synergistic effect is also present in this catalyst. Thus, it is the Pd precursor and not the impregnation sequence of the metals (coimpregnation or sequential impregnation) that is responsible for the synergistic effect reported in our previous paper [9] with the bimetallic Pd–Rh catalysts prepared by sequential impregnation.

4. Conclusions

The *in situ* study by FTIR of the CO species adsorbed on oxidized bimetallic Pd–Rh/SiO_2 catalysts during the reaction of CO with CO_2 in an oxidizing atmosphere, indicates that the catalysts prepared by the method of sequential impregnation show a lower degree of surface oxidation than those prepared by coimpregnation with the inorganic precursors $RhCl_3$ and $PdCl_2$. The two methods of impregnation lead to the existence of oxidized Rh on the surface of the bimetallic catalyst. However, in the sequential impregnation method the Pd surface is more reduced than in the bimetallic catalyst prepared by coimpregnation of the inorganic precursors. The simultaneous existence of reduced Pd and oxidized Rh that occurs in the catalysts prepared by sequential impregnation allows the occurrence of the synergistic effect proposed by Oh and Carpenter for the Pt–Rh system.

On the other hand, it has been shown that the lower degree of oxidation of the Pd in the catalyst prepared by sequential impregnation is mainly due to the fact that the Pd in those catalysts comes from the organic precursor palladium acetylacetonate. The fact of coimpregnating or sequentially impregnating both metals is not responsible for the existence or nonexistence of the synergistic effect, and synergism is seen to exist in both cases if the organic Pd salt is used as the precursor.

This is an interesting observation, since it shows that the oxidizing conditions of the Pd surface can be controlled by the appropriate selection of the precursor metal during the impregnation step.

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