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LETTERS TO THE EDITORS

IR Spectra of CO Adsorbed on Metals: Comments on the Paper "On the Electronic Competition Effect upon CO Adsorption on Metals" by H. A. C. M. Hendrickx, C. des Bouvrie, and V. Ponec

In (*1*) a comparison of the IR study results of CO adsorption on Pd/SiO_2 and literature data for Pd(111) and Pd(100) monocrystals have allowed those authors to conclude that:

(a) a coverage-dependent frequency shift of CO absorption bands is much smaller for dispersed Pd than for monocrystals (25–33 and ~100 cm^{-1}, respectively), and

(b) in contrast to monocrystals, the whole shift on Pd/SiO_2 is a result of dipole–dipole coupling between the adsorbed molecules.

The dynamic component of shifts is the same in both cases (~30 cm^{-1}). It was suggested that the excessive shift for monocrystals is due to "changes in the adsorption sites occurring with increasing θ(CO) on flat metal surfaces, but this effect is absent on curved rough surfaces of small metal particles." But it is essential to point out that the frequencies at $\theta(CO) = 1$ for disperse and bulk systems are rather close and the main differences (~100 cm^{-1}) have been found for ν(CO) at low coverages. We believe that these values ("singletones") are important characteristics, since they are determined only by the CO binding mode rather than by coverage-dependent factors (both dynamic and static). Thus the singletone may be considered to be a characteristic of electron state of the metal surface sites. On the basis of the difference of singletones in (*1*) one may conclude that surface adsorption site states differ for bulk Pd and small metal particles. This conclusion, if true, is very important for the chemistry of supported metals and therefore it requires careful experimental examination.

In this connection, it should be noted that the correctness of ν(CO) values at $\theta(CO) \rightarrow 0$ in (*1*) is doubtful. Indeed, they differ from previous data for supported Pd (*2*), in particular Pd/SiO_2 (*3, 4*). In these papers ν(CO) at low coverages were much lower (while $\Delta\nu$ 2.5–3 times more) than in (*1*). Obviously, it is impossible to measure the ν(CO) values less than the true singletone, but the inverse is quite possible. This is why the lowest value should be preferred to be true if one compares the various data. Most typically the overestimated values of singletone could be obtained as a result of heterogeneous CO distribution in the sample pellet. Due to the high sticking probability practically the whole CO portion adsorbs at the outer layer of the pellet at room temperature, the local coverage appears to be rather high. Therefore one can find the bands at higher frequencies as compared with the true singletone even at low integral coverage. Palazov *et al.* were the first who paid attention to this feature and proved it just for Pd/SiO_2 (*4*). Later similar results were obtained for other systems, for example, Pt/Al_2O_3 (*5*). Thus, the measurement of singletones for supported metals is an important but a rather difficult experimental problem which requires both special methods and sensitive techniques.[1] This is

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[1] In addition, it is important to recognize that due to the inhomogeneity of supported systems the chance exists that the singletone obtained corresponds to the minor part of specific particles (or crystallographic faces) with the maximum heat of adsorption. We are going to discuss this question in following publications.

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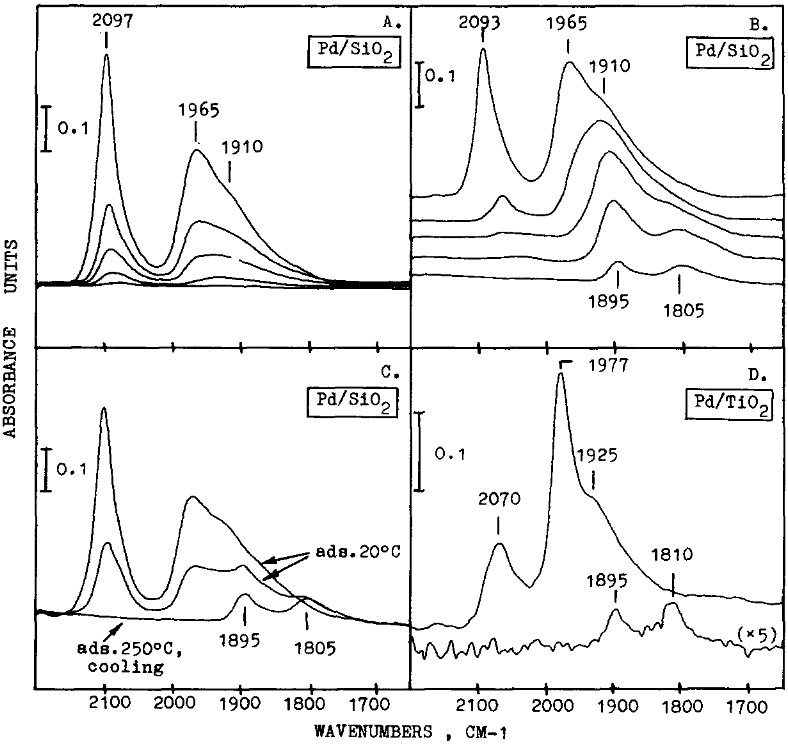

FIG. 1. IR spectra of CO adsorbed on Pd/SiO_2 (A–C) and Pd/TiO_2 (D), background subtracted (2 wt% Pd, impregnation by acetone solution of $Pd(OAc)_2$, reduction *in situ* at 350°C in H_2, $\bar{d} \simeq 35 \div 60$ Å): (A) 20°C, increasing coverage; (B) spectra at 20°C after desorption at 20, 150, 250, 300, and 350°C; (C) adsorption at 250°C ($\theta \simeq 0.1$), cooling to 20°C, adsorption at 20°C, increasing coverage; (D) adsorption at 200°C, different coverages (spectra at 200°C).

the reason why extremely low integral coverages are required to obtain a true singletone in the case of CO adsorption at room temperature (≤ 0.01, (*6*)). In addition, reliable data can be obtained even at relatively high θ(CO), when desorption at increased temperature is studied, since a more uniform CO distribution is achieved in this case. Agreement between the values measured in different conditions may be taken as evidence for their validity.

Measurements of singletones as a function of metal/oxide system parameters (particle size, mode of deposition, nature of support) have been one of our objectives, with supports being SiO_2, Al_2O_3, and transition and rare earth oxides (*15*). The study of a series of systems has shown that singletones of appropriate carbonyl types for Pd, Rh, and Pt are close to those for monocrystals and, in fact, are independent of nature of support and preparation conditions. For example, Figs. 1 and 2 summarize the IR data of CO adsorption on Pd and Rh catalysts. The bands for Pd shift to ~1890, 1805 cm^{-1} when $\theta(CO) \rightarrow 0$, these values appear to be close to singletones for Pd(100), Pd(111), respectively, (*7*) and correspond to two- and three-bonded CO.[2] In the case

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[2] Figure 1A shows the adsorption experiment similar to that in (*1*); Fig. 1B displays the spectra from the high temperature desorption which allows us to obtain the singletones. Figure 1C is presented to prove that this treatment does not lead to surface modification. It is clear, since the intensity of 1890 and 1805 cm^{-1} bands decreased progressively and disappeared during CO adsorption at 20°C; the final spectrum is similar to that at Fig. 1A.

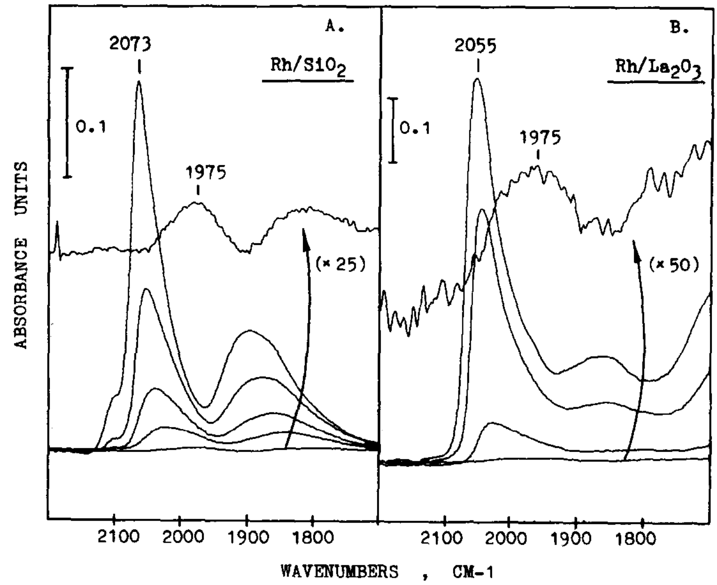

FIG. 2. IR spectra of CO adsorbed on Rh/SiO_2 (A, 1 wt%) and Rh/La_2O_3 (B, 1.1 wt%) at 20°C, increasing surface coverage (pretreatment condition—see (*6*)).

of Rh the linear carbonyl bands appeared at ~1975 cm^{-1} and shifted to 2060–2070 cm^{-1} (*6*) when CO coverage increased, this singletone value being close to that reported for Rh(111) (*9*). (In the recent paper (*14*) the authors took the value 2015 cm^{-1} as a singletone for Rh/SiO_2, but we think that it is also overestimated.) Note that at 20°C the true singletones have been measured at $\theta \leq 0.01$, which appeared to be possible with the use of the high sensitive technique (IFS-113v spectrometer, "Bruker," MCT detector). There exists a good agreement of these values with those obtained during desorption. Note in this connection, that the minimum coverage in (*1*) was as high as 0.15, whereas ν(CO) values at θ(CO) = 0 have been obtained by extrapolation. But this procedure seems to be incorrect. Besides the former reason (inhomogeneity of CO distribution), it is essential that a rather great band shift is known even for monocrystals just at low coverages (*7, 8*). The possible reasons for such behavior have been discussed in (*1*) and those conclusions seem to be quite valid. However, no experiments have been performed in (*1*) to exclude similar behavior for supported systems. The same is true for isotopic dilution experiments, where the most diluted mixture contains ~20% of ^{12}CO. So these results should be treated with care too in spite of the fact that isotopic experiments were performed at the integral $\theta = 1$ and thus the factor of inhomogeneity of CO distribution could not operate.

So there is no basis to assume any specificity in CO adsorption on small Pd particles compared with monocrystals.

In conclusion, it should be noted that the problems under discussion are related directly to the question of what kind of information could be obtained by IR spectroscopy of CO adsorption on supported metals. As stated above, the general characteristics of the metal are the singletone frequency (electron state of the surface metal atoms) and coverage-dependent ν(CO) shift (the nature and extent of lateral interactions). Since both parameters are close for metals supported on inert oxides

(SiO_2, Al_2O_3) and for monocrystals, it is clear that supporting of metals did not affect notably their properties in CO adsorption. Furthermore, the singletone did not change even for the oxides of transition and rare earth elements, so it is obvious that the electronic state of metal surface is not affected either. As for the coverage-dependent shifts (or ν(CO) at θ(CO) = 1) for the given metal, these values are somewhat different (~10–15 cm^{-1}) for various supports but never exceed that for monocrystals. So we believe that this is the result of a "geometric effect," namely the difference in the size of islands on metal surfaces accessible for CO adsorption since the ν(CO) shift depends on the number of neighboring CO molecules. The simplest example of this dependence could be observed when the size of islands was defined by the metal particle diameter. Indeed, for SiO_2- and Al_2O_3-supported catalysts it is known that the particle size affects the ν(CO) at θ(CO) = 1 (*10*). However, other reasons which give the same result also exist. For instance, there may exist other molecules on the metal surface, carbon deposition, or the recently proposed partial blocking of metal by suboxide fragments after the high temperature reduction of catalysts (*11–13*). Our studies of these problems indicate (*15*) that IR spectroscopy gives an important and, possibly, unique information about metal surface states.

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