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Infrared Spectra of Carbon Monoxide Adsorbed on Silica-Supported PdAg Alloys

The formation of alloys of a Group VIII and a Group IB metal leads to important changes in catalytic selectivity (*1–3*). Two identified causes of this phenomenon are the geometrical "ensemble effect" and the electronic "ligand effect" of alloy catalysts (*4*). In order to discriminate between these two effects, Soma-Noto and Sachtler (*5, 6*) studied the infrared spectra of CO on supported PdAg alloys using a conventional spectroscopic technique. They observed a pronounced change in relative intensities of the ir bands. Whereas on pure Pd the band prevailed that is usually attributed to the "multisite" or "bridge" complex of CO, in which this molecule is perpendicular to the surface and equidistant to two, three, or four surface Pd atoms, the addition of Ag to Pd strongly favored the formation of the linear CO complex, in which the CO molecule is located on top of one Pd atom. The changes in band position due to alloying were far less pronounced than the changes in intensity; with the technique used, it was not certain whether the frequency shifts exceeded those due to the increased average distance between CO molecules adsorbed on Pd atoms interdispersed with Ag atoms. The authors concluded that in this adsorption, the geometric ensemble effect prevails over the ligand effect. They arrived at similar results and conclusions in their study of CO complexes on NiCu alloys (*7*).

More recently, Dalmon *et al.* (*8*) studied the adsorption of CO on SiO_2-supported NiCu alloys by using a more sophisticated ir technique and making magnetic investigations. These authors confirm the pronounced increase in intensity ratio of the ir bands due to the linear and multisite complexes of CO, but they also state that alloying Ni with Cu results in a significant band shift which is clearly in excess of the one caused by lowering the degree of coverage of the surface with CO. They conclude that in addition to be geometric effect an electronic interaction is operative. They also mention that the concentration of the bridged CO complex is lower than the concentration of surface Ni_2 pairs, calculated on the basis of simple statistics.

The two apparently conflicting conclusions initiated the present study. We used the $PdAg/SiO_2$ samples previously prepared and studied by Soma-Noto and Sachtler and measured the ir spectrum of CO adsorbed on these samples with the same spectrometer (Digilab FTS 14, equipped with a Fourier transformer) as the one used previously by Dalmon *et al.* (*8*).

The samples were reduced in a stream of hydrogen at 350–400°C for 10 hr and subsequently evacuated at the same temperature for 3 hr. Then the spectrum was recorded and used as a reference, thus eliminating all bands due to the support from the spectra obtained after admitting CO at room temperature.

The results in Fig. 1 show that on pure Pd/SiO_2 two bands prevail: these are a weak band above 2000 cm^{-1}, conventionally ascribed to the linear Pd–CO complex, and a much more intense band below 2000 cm^{-1}, attributed to the "bridge"

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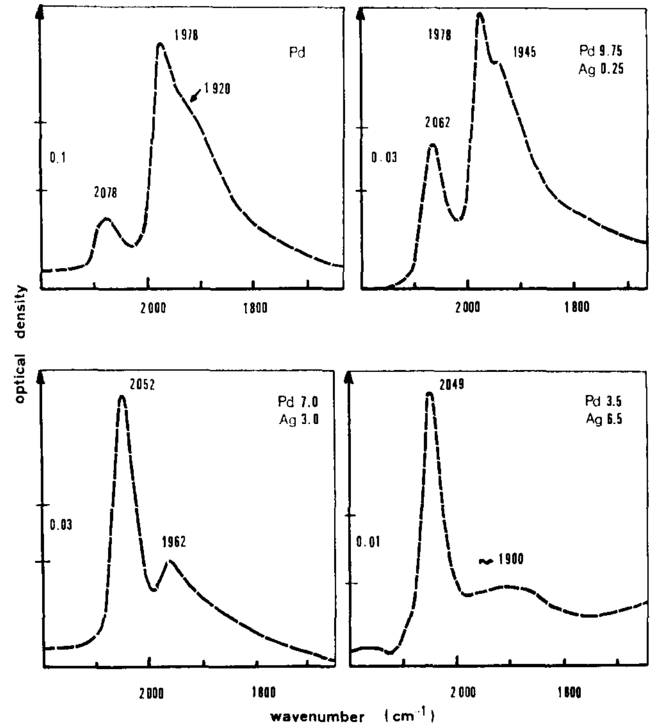

FIG. 1. Infrared spectra of CO irreversibly adsorbed at room temperature on SiO_2-supported Pd–Ag alloys.

or "multisite" complex. Upon alloying Pd with Ag, the most spectacular phenomenon visible from the spectra is the dramatic change in relative intensities, greatly favoring the linear complex confirmatory with previous results (*5–7*). In Fig. 2 the

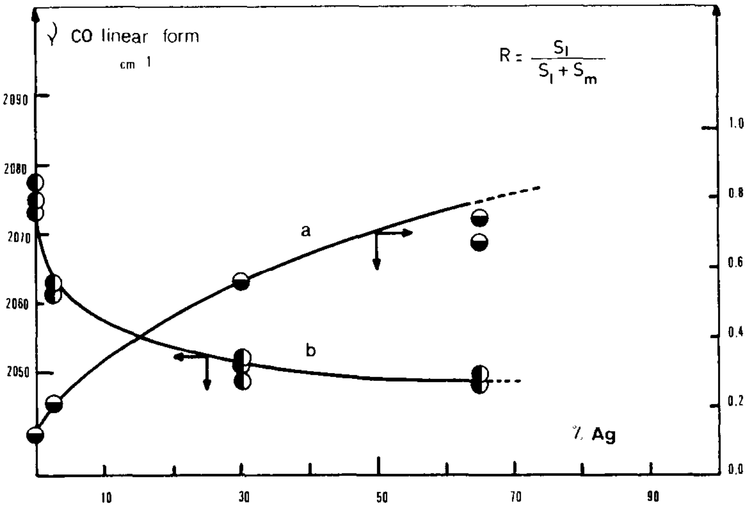

FIG. 2. (a) Ratio $S_l/(S_l + S_m)$ as a function of the alloy composition [S designated as the integrated optical densities for the linear form (S_l) and for the multicentered form (S_m)]. (b) CO frequencies of the linear species as a function of the alloy composition.

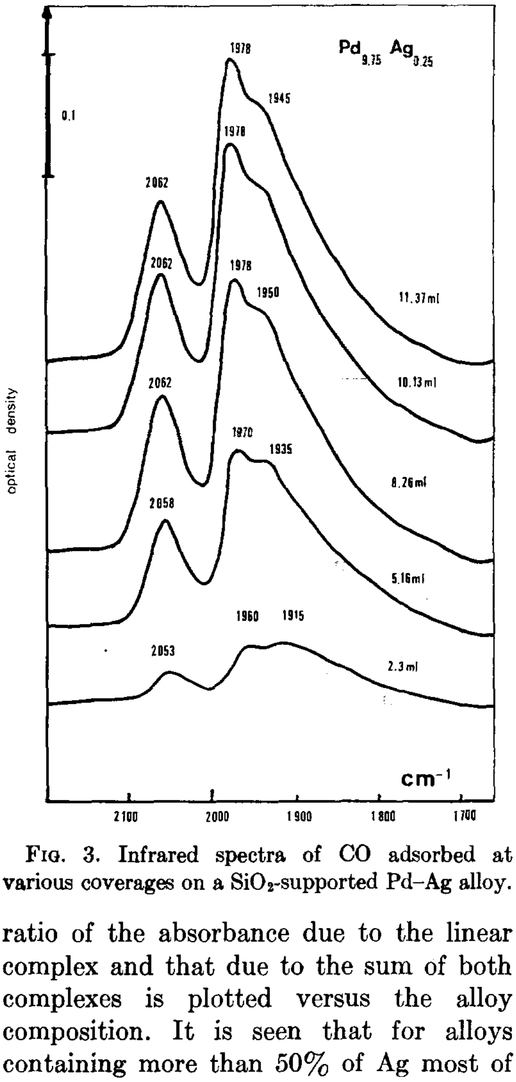

FIG. 3. Infrared spectra of CO adsorbed at various coverages on a SiO_2-supported Pd–Ag alloy.

ratio of the absorbance due to the linear complex and that due to the sum of both complexes is plotted versus the alloy composition. It is seen that for alloys containing more than 50% of Ag most of the chemisorbed CO is present in the linear form.

Even if we accepted that the surface of the alloy particles will be much richer in Ag than their bulk *(9)*, and if we take into account that the specific absorbance of the linear complex exceeds considerably that of the multisite complex *(6, 10)*, it remains difficult to reconcile this high preference for linear CO with a model in which only those Pd atoms which are completely surrounded with Ag atoms adsorb CO in the linear form.

Also trivial geometric causes such as a drastic change in particle size or shape can be ruled out on the basis of the electron microscopic and X-ray diffraction analysis of these samples *(5)*. It follows that ensembles of two, three, or four Pd atoms adjacent to one or several Ag atoms chemisorb CO in the linear form, although the geometric condition for a multisite complex is fulfilled. A challenging question, though beyond the scope of this Note, is why the interaction of Ag with Pd has this "linearizing" effect.

As to the frequency shift, the following is reported. According to the (σ, π) model normally used to explain the formation of metal carbonyls and the chemisorption of CO by metals, π back-donation is responsible for the major part of the bond energy. Electron donation to the adsorbing metal should then shift the CO vibration to lower frequency values as a result of increased π back-donation. Indeed, Fig. 2 shows that the ν CO frequency of the adsorbed species decreases monotonically with increasing Ag content. If alloying Pd with Ag were the sole cause of the shift, one might explain this phenomenon by assuming that an increased electron density on the Pd surface atoms results in an increased Pd → CO back-donation. Such a model would not be in disagreement with magnetic results *(11)* which, however, leave open two possibilities: these are donation of Ag *s* electrons to the Pd *d*-band, or shifting of Pd *s*-electrons to the Pd-band, as is in fact found for isolated Pd atoms, e.g., in Pd vapor.

When all the Pd atoms of an alloy particle surface are covered with CO, the average distance between neighboring CO_{ads} molecules will be larger than for a surface of Pd, undiluted with Ag and fully covered with CO. As a consequence, the mutual depolarization of CO dipoles will be lower for the alloy than for pure Pd. Furthermore, the shift of *s*-electrons from the surface towards CO_{ads} due to back-donation will lead to a lowering of the *s* electron density of the metal surface, and this electron drainage per surface atom will, of course, be lower for a Pd–Ag alloy where only the Pd atoms carry CO molecules, than for a Pd surface at full coverage. Also this effect might cause a shift in ir bands and will then contribute to the total band shift actually observed. In view of this we have studied the band shift with coverage by admitting successive doses of CO at room temperature to a sample. The results in Fig. 3 show that increasing the adsorbed quantity of CO from 2.3 to 11.37 ml/g of Pd causes a frequency shift of only 9 cm^{-1}, whereas increasing the overall silver content from 0 to 65% shifts the same frequency from 2078 to 2049 cm^{-1}. From these results we conclude that also for this alloy system a geometric and an electronic effect are operative.

Upon examining Fig. 3 it is also clear that at low coverages of Pd with CO the band below 2000 cm^{-1} actually consists of two bands of comparable intensities, located at 1960 and 1915 cm^{-1}. In coordination chemistry it has been shown that the degree of back-donation increases with the number of metal atoms involved in bonding one CO molecule. For two-center-bonded CO the CO frequencies thus vary between 1850 and 1750 cm^{-1}, but for three-center-bonded CO they vary between 1730 and 1620 cm^{-1} (*12*). Shoulder formation in the band below 2000 cm^{-1} had previously been reported by other authors (*13*). It might be indicative of the existence of a nonnegligible portion of CO molecules bonded to three metal atoms in addition to the CO molecules "bridging" two Pd atoms only. Although the ratio of linear to multisite bonded CO changes only little with the degree of coverage, it is noteworthy that the species bonded to more than two metal atoms prevails at low coverage, showing that this species is the most stable complex of CO on Pd.

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