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Infrared Spectra of Carbon Monoxide Adsorbed on Silica-Supported Nickel–Copper Alloys

In our previous report on supported Pd–Ag alloys (*1*) we showed that on Pd metals the concentration of the bridged CO complex decreased much more rapidly with increasing Ag content than that of the linear complex. On the other hand the band frequencies and the heat of adsorption of CO remained virtually unchanged in the whole composition range of alloys. From these results we concluded that in the case of CO adsorption on the Pd atoms of Pd–Ag alloys the "ligand effect" is relatively unimportant, but the geometry of the alloy surface is decisive for the relative abundance of the bridged and linear CO complexes.

Ni–Cu and Pd–Ag alloys show besides certain similarities also some differences in their electronic structures. In particular, the population of the *d*-electrons in Ni is little influenced by Cu in Ni–Cu alloys (*2*) but in Pd–Ag the hole of the Pd *d*-state is filled by alloying with Ag (*3*). It is, therefore, interesting to see how the electronic structure of bulk alloys influences the CO adsorption on the alloy surface. A second characteristic difference between the two alloys is that Ni–Cu unlike Pd–Ag has a miscibility gap (*4, 5*). For equilibrated Ni–Cu films the surface composition was consequently found to be constant over a wide composition range of the alloy (*6*). It is not known, however, whether this equilibration will also be possible for supported alloys where the alloy particles are very small and not in physical contact with each other. The ir spectra in combination with X-ray data and manometric determinations of adsorbed quantities should provide information on the phase behavior and surface composition of these supported alloys.

Silica (Aerosil) supported Ni–Cu alloy catalysts were prepared by impregnation from mixed aqueous solutions of Ni- and Cu-nitrates. The samples were subsequently dried and reduced at 450°C for 18 hr with flowing hydrogen. For the infrared spectral measurement, the samples were pressed into a disc and reduced at 350°C for 3 hr in the cell and evacuated at the same temperature for 2–3 hr or for 18 hr to complete the annealing of the alloy. The remainder of the experimental procedure was the same as described previously (*1*).

Lattice constants and particle sizes of Ni–Cu alloys were calculated from the X-ray diffraction data of the (111) and (200) alloy peaks. The lattice constants of the alloys containing more than 70% Ni were found to change linearly with composition but the alloys with less than 50% Ni were found to consist of two phases, viz, a Cu-rich alloy (about 95% Cu) and a Ni-rich alloy (about 65% Ni). While their lattice constants remained constant with metal composition, the relative amounts of the two alloy phases changed. The apparent particle sizes measured by line broadening were constant for the Ni-rich alloys at 120–150 Å in the whole composition range, but those of the Cu-rich alloys were much larger, varying from 300 to 600 Å depending on the Ni content.

The segregation in these two phases evidently does not reflect the equilibrium situation of bulk Ni–Cu alloys. We presume that it is a consequence of the preparation method by impregnation. One can visualize, e.g., that while the metal salt solution is drying, the two salts are precipitated on certain SiO_2 centers in the order of their relative solubility products. The composition of the precipitated nitrate particles might then determine the Ni/Cu ratio in

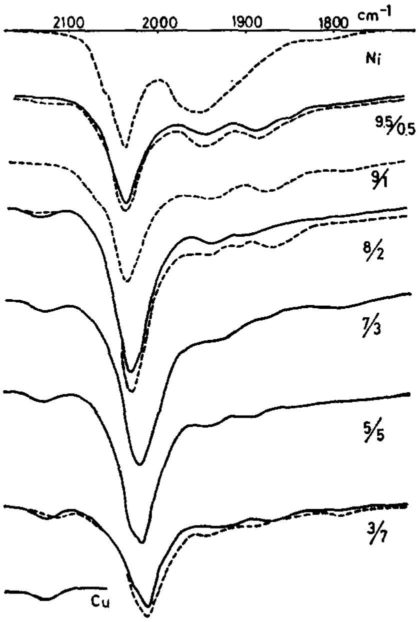

FIG. 1. Infrared spectra of CO adsorbed on Ni–Cu alloys around 0.02 Torr CO pressure: (——) the alloys were evacuated 18 hr at 350°C before CO adsorption; (- - -) the alloys were evacuated 2 hr at 350°C before CO adsorption.

the alloy crystals after reduction. This question, however, will not be further discussed in this Note.

Infrared spectra of CO adsorbed on alloys were measured in the CO pressure range of 10^{-4}–10 Torr at room temperature. Figure 1 shows the spectra for various alloys at about 0.02 Torr CO pressure. In these spectra two features are distinguished, namely, the high frequency bands (above 2000 cm^{-1}) and the low frequency bands (below 2000 cm^{-1}). On Ni, the absorbance of the high and the low frequency bands are comparable, but on the alloys the intensity of the low frequency bands decreases markedly with increasing Cu content. (The frequency of the main band on the alloys is about 2020 cm^{-1} and increases with CO coverage.) The frequencies of CO bands on all alloys remain virtually unchanged with metal composition. These results, i.e., a drastic change in absorbance ratio but no change in band position, are analogous to those reported for CO on Pd–Ag alloys.

While the bands discussed so far are all attributed to CO molecules adsorbed on the Ni atoms of the alloys, a band of CO adsorbed on Cu metal appeared at about 2130 cm^{-1} at a CO pressure exceeding 6×10^{-3} Torr at room temperature. Upon pumping it disappeared. At high CO pressures the frequency and the band intensity changed only little. This weak and reversible band was also observed on Cu-rich alloys and is ascribed to the adsorption of CO on the Cu atoms in the alloy surfaces. Its intensity was always an order of magnitude below that of the 2020 cm^{-1} band ascribed to the adsorption of CO on Ni atoms.

The ratio of the absorbance between the high and low frequency bands assigned to CO adsorbed on Ni atoms is shown in Fig. 2. It increases strongly with increasing Cu content in the alloys, but becomes constant for the alloys above 20% Cu. The adsorbed amount of CO per alloy surface area shows a constant value on alloys with less than 90% Ni. This result suggests that these alloys have a constant composition

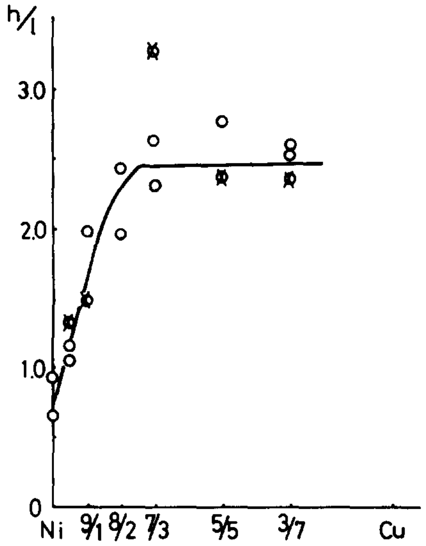

FIG. 2. The ratio h/l of the absorbance of the high frequency bands (>2000 cm^{-1}) and the low frequency bands (<2000 cm^{-1}) $P_{CO} \sim 0.02$ Torr: (⊗) the alloys were evacuated 18 hr at 350°C before CO adsorption; (○) the alloys were evacuated 2 hr at 350°C before CO adsorption.

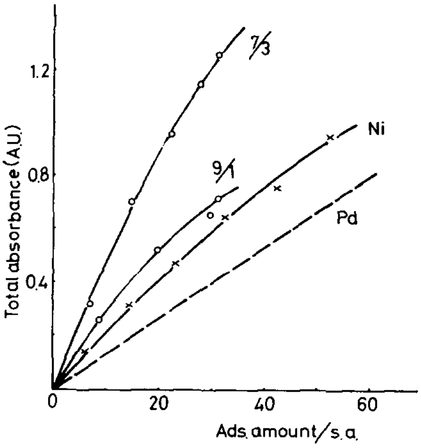

FIG. 3. Total absorbance of CO adsorbed as a function of CO coverage $h/l \sim 4$ on $Ni_{0.7}Cu_{0.3}$ alloy; $2.3 \sim 1.6$ on $Ni_{0.9}Cu_{0.1}$ alloy; ~ 1 on Ni; <0.1 on Pd.

of the surface. For the Cu-rich alloys where two phases coexist we assume that the observed bands are due to CO adsorbed on the Ni-rich phase as this phase with the markedly smaller particle size exhibits the larger surface area.

Specific intensities of CO bands on Ni and alloys were examined, measuring the adsorbed amounts volumetrically (P_{CO} eq. < 0.01 Torr). As is shown in Fig. 3, the specific intensity depends on the alloy composition. On the $Ni_{0.7}Cu_{0.3}$ alloy, the absorbance of the low frequency bands was less than 20% of that of the high ones, and the specific intensity was almost three times larger than that for CO on Pd (*1*) where the high frequency bands were negligible. This result shows the large difference in the specific intensity of the high frequency bands and that of the low frequency bands. A similar behavior has been suggested also in the case of Pd–Ag alloys. This large difference of the specific intensities prevents the estimation of the adsorbed amount of CO from the total absorbance.

For one absorption band, the major one at 2020 cm^{-1} on alloys, the decrease of the absorbance was measured upon evacuation around 190°C. From the measured desorption rate ($-d\Phi/dt$) and the desorption temperature T, the free energy of activation for desorption $\Delta G^{\ddagger}$ was calculated using the equation:

$$-\frac{d\Phi}{dt} = \frac{kT}{h}\Phi \exp\left(-\frac{\Delta G^{\ddagger}}{kT}\right).$$

A constant value $\Delta G^{\ddagger} = 35$ kcal/mole was found for all alloys including pure Ni. This shows that the intrinsic character of each Ni atom in the Ni–Cu alloy surface does not change appreciably with alloy composition. The strength of the Ni–CO bond is not much affected by the neighbors of the Ni atom. A completely analogous result was obtained in the case of Pd–Ag alloys.

In conclusion, the absorption bands of CO adsorbed on Ni–Cu alloys show a behavior similar to that observed on Pd–Ag alloys. For both alloys the intensity of the low frequency bands below 2000 cm^{-1} decreased quickly with increasing concentration of the Ib metal. For Ni–Cu the major band was at 2020 cm^{-1} while for Pd–Ag the corresponding band frequency was 2050 cm^{-1}. This high frequency band at 2020 or 2050 cm^{-1} is due to a linear bonding CO with Ni or Pd, while the low frequency bands are due to a bridge-bonding CO, so the arguments for Ni–Cu are the same as those discussed for Pd–Ag in our previous paper (*1*). The constancy of the CO band frequency in the whole composition range shows that in the case of CO adsorption the intrinsic character of the adsorbing transition metal atom in both Ni–Cu or Pd–Ag alloy surfaces is not changed appreciably by a "ligand effect" of the nearest neighbors in the solid. The relative concentration of the two adsorption states for CO (linear, bridged) are determined predominantly by the geometric condition of the alloy surface, since every transition metal atom can form a linear complex with CO but pairs of adjacent transition metal atoms are required for the formation of the bridged complex.

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