JOURNAL OF CATALYSIS 37, 391–395 (1975)

Chemisorption of Olefins on Evaporated Transition Metal Films; Infrared Studies

I. Ethylene and Propylene on Nickel, Cobalt, Rhodium and Platinum

J. WOJTCZAK,[1] R. QUEAU AND R. POILBLANC[2]

Groupe d'etude et d'application des complexes métalliques, Laboratoire de Chimie de Coordination du CNRS, 38, rue des Trente-six ponts, 31 Toulouse, France

Received December 7, 1973; revised September 16, 1974

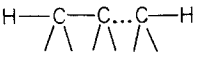
Infrared studies of carbon monoxide and olefins simultaneously chemisorbed at room temperature on transition metal films point to the fact that on evaporated nickel or cobalt films previously covered with CO, olefins cause CO desorption and form surface species, which after treatment by hydrogen are easily removed from the surface by readsorption of CO. There is also a small amount of species, perhaps high polymers, which remain on the surface after the treatment by hydrogen and reexposure to CO. On films previously covered with hydrogen, chemisorbed olefins are considered to form some polymeric species, which remain on the surface after treatment by hydrogen; the further chemisorption of CO is then impossible. These experimental findings may be interpreted in terms of CO acting as a good inhibitor of polymerization on nickel and cobalt films. The cases of rhodium and platinum films give less significant results.

INTRODUCTION

The mechanism of the chemisorption of olefins on metals is not well understood. However, two kinds of chemisorption are commonly discussed. Chemisorption can be nondissociative, the olefin molecules being bonded to the metal without loss of hydrogen atoms. Chemisorption can also be dissociative, the olefin losing some hydrogen atoms, and the residue being bonded to the metal by several M–C bonds.

Nondissociative chemisorption would be expected to prevail at low temperature, in the case of a high surface coverage (*1*) and when hydrogen is preadsorbed (*2*). However, by some means or other, chemisorption of unsaturated hydrocarbons forms radicals on the surface (*3,4*) and polymerization can occur (*1,3,5*).

Eischens and Pliskin (*2*) and Sheppard and Ward (*6*) have indicated from infrared studies of chemisorption of ethylene and acetylene on nickel (*2*) and acetylene on nickel and platinum (*6*) that polymers M–$(CH_2)_{n-1}$–CH_3 with $n \geq 4$ occur. Bond (*3*) has proposed that in the case of the loss of a great number of hydrogen atoms polymers like



can be produced, which are bonded to the metal surface through many M–C bonds. However, the existence or the nonexistence of high polymers formed during chemisorption of olefins on evaporated metal films has not been clearly demonstrated.

Previous ir studies of chemisorbed CO on transition metal films (*7,8*) have shown

[1] Present address: Instytut Chemii U. M. K., 87100 Torun Bielany, Poland.

[2] To whom correspondence should be addressed.

that, by observing the behavior of the CO stretching frequency, CO can be used as an indicator (*9*) of the presence of other electron donor molecules or electron acceptor molecules chemisorbed simultaneously. The same concept has also been used by Primet *et al.* (*10*) to rationalize several observations on supported platinum catalysts. The changes of the intensity of the ir absorption band can indicate the CO surface coverage changes. Using these properties of CO an attempt was made to ascertain whether on metal films, chemisorbed olefins can polymerize to form previously described species (*2,6*), and whether high polymers occur. Zakharov *et al.* (*11*) have shown that Lewis bases like CO and PH_3 can inhibit olefin polymerization on various catalysts. The possible occurrence of such a phenomenon on metal films has now been investigated. Experiments were performed on the *assumption* that after treatment by hydrogen, monomers, or polymers with relatively few carbon atoms, would be easily replaced by carbon monoxide. It was also assumed that, on the contrary, polymers of high molecular weight and low vapor pressure bonded to the surface via numerous M–C bonds would not be desorbed at room temperature, and would screen the film surface from CO. The manner in which these assumptions are substantiated by our results is discussed. The cases of ethylene and propylene chemisorbed on nickel, cobalt, rhodium and platinum are described.

EXPERIMENTAL METHODS

Technique. The preparation of the metal films has been previously described (*7*). A small sample of the appropriate metal is evaporated from a tungsten filament on to NaCl windows, in the presence of a small amount of CO or H_2. Two modes of preparation have been used; (i) either 10^{-1} Torr of CO, a condition of priori unfavorable to polymerization (*11*), or (*ii*) 10^{-1} Torr of H_2, a condition not unfavorable to polymerization. A new cell made of Pyrex glass has been designed to eliminate the vacuum grease from ground glass joints and stopcocks. The vacuum tightness between the body of the cell and the salt windows is realized with a Viton O-ring positioned with a metal flange as shown in Fig. 1. Joints and stopcocks from West Glass are made only of Pyrex glass, Teflon and Viton.

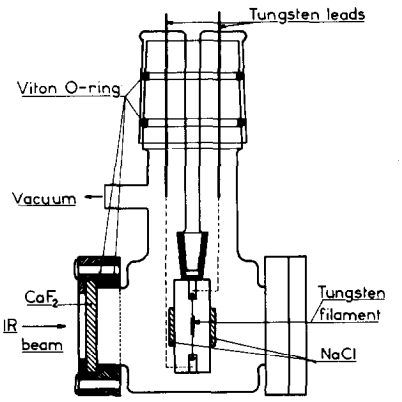


FIG. 1. Infrared cell.

Materials. Nickel, cobalt, rhodium and platinum were obtained from Johnson and Matthey or Comptoir Lyon Alemand as 0.1 mm diameter high purity wire (99.99%). Tungsten was obtained from Alfa Inorganics. Carbon monoxide (99.995%), ethylene, propylene (99.99%) and hydrogen (99.999%) were obtained from Air Liquide and were used without further purification.

Recording spectra. Infrared spectra of chemisorbed molecules were recorded at room temperature on a Perkin-Elmer Model 225 double beam grating spectrometer in the region of the CO stretching frequencies (2200–1600 cm^{-1}) and in the region of the C–H stretching frequencies (3200–2700 cm^{-1}). The transmittance of the cell is about 30% at 2000 cm^{-1}.

Procedure. After preparation according to mode (i) or mode (ii) films have been submitted at room temperature to the following sequence:

1. Addition of 700 Torr of olefin for 14 hr.
2. Addition of 700 Torr of CO for 8 hr.
3. Addition of 700 Torr of H_2 for 3 hr.
4. Addition of 700 Torr of CO for 3 hr.

After each step the gas phase of the cell was evacuated to eliminate its infrared spectrum. The reaction times were chosen so as to reach a stationary state; prolongation of this time produced no change in the infrared spectra of chemisorbed species.

RESULTS

Infrared spectra of chemisorbed CO on nickel, cobalt, rhodium and platinum films evaporated in CO are in perfect agreement with our previous results (*7*) (Table 1). For films evaporated in H_2, subsequent addition of CO produced infrared spectra analogous to those obtained on films evaporated in CO.

Nickel and cobalt films evaporated in CO (mode i). Additions of ethylene or propylene (step 1) to nickel and cobalt films carrying presorbed CO produce a shift to lower frequencies of the CO stretching frequencies (Table 2) and a weakening of the intensity of the ir bands. Subsequent addition of CO (step 2) produces no changes. On the other hand, after addition of H_2 followed by CO (steps 3 and 4), the intensity of the CO bands greatly increases; the CO stretching frequency also increases, but, the $\bar{\nu}_{CO}$ does not reach its initial value (Table 2). The corresponding spectra are shown in Fig. 2 for ethylene adsorption; for propylene the spectra are similar and have not been reproduced. After step 1, in the $\bar{\nu}_{CH}$ stretching region, bands have been observed only in the case of propylene on nickel. After 1 hr, these bands are located at 3020, 2920 and 2850 cm^{-1} (Fig. 3). After 3 hr the 3020 cm^{-1} band disappears and the intensities of the 2920, and 2850 cm^{-1} bands decrease.

TABLE 1
CO STRETCHING FREQUENCIES OF CHEMISORBED CO ON FILMS EVAPORATED IN 0.1 TORR OF CO[a]

Nickel	Cobalt	Rhodium	Platinum
A 2035	A 1960	A 2015	A 2040
B 1890	B 1815	B 1860	

[a] All frequencies in cm^{-1}. A and B are used as labels for the different bands.

TABLE 2
SHIFTS TO LOWER FREQUENCIES OF THE CO STRETCHING FREQUENCIES OBTAINED BY ADDITION OF ETHYLENE[a]

	Nickel	Cobalt	Rhodium	Platinum
Δ_1	A 35	A 20	A 10	A 5
	B 85	B 45	B 10	
Δ_2	A 30	A 5	A 10	A 5
	B 40	B 25	B 10	

[a] All shifts in cm^{-1}. The labels A and B refer to the bands quoted in Table 1. Δ_1, after addition of ethylene; Δ_2, after addition of ethylene + H_2 + CO.

Nickel and cobalt films evaporated in H_2 (mode ii). After prior exposure to olefin (step 1), the addition of CO (step 2) does not produce detectable infrared absorption bands of chemisorbed CO. However, after addition of H_2 and CO (steps 3 and 4) on nickel, very weak infrared bands appear at 2000 and 1850 cm^{-1} for ethylene (Fig. 4) and propylene. In the corresponding experiments on cobalt no bands have been detected. In all cases no significant infrared bands have been observed in the $\bar{\nu}_{CH}$ stretching region.

Rhodium and platinum films evaporated in CO (mode i). Addition of olefins to these films produces a very weak decrease of the intensity of the CO infrared absorption bands, and a weak lowering of the $\bar{\nu}_{CO}$ stretching frequencies. After addition of H_2 and CO (steps 3 and 4) no significant changes were observed (Table 2, Fig. 2).

Rhodium and platinum films evaporated in H_2 (mode ii). After evaporation of the films especially in the case of platinum, small amounts of chemisorbed CO have been observed. However, the surfaces are

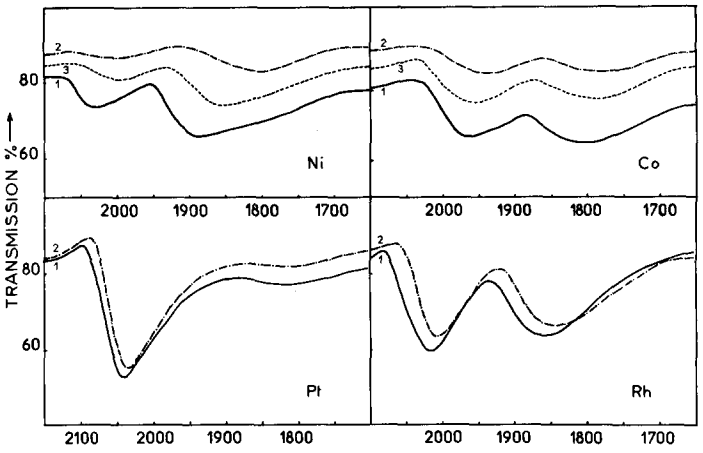


FIG. 2. Infrared spectra of chemisorbed CO; addition of ethylene. Frequencies in cm^{-1}. (1) After evaporation; (2) after addition of ethylene; (3) after addition of ethylene, H_2 and CO. In the case of Rh and Pt these spectra are identical to spectra 2.

not completely covered with CO, as can be shown by the fact that the infrared absorption bands increase in intensity when CO is added into the cell. After step 4, in the case of platinum, no modifications of the initial spectrum were observed (2030 cm^{-1}); in the case of rhodium a weak increase of the band intensities occurs (2000, 1840 cm^{-1}) (Fig. 4).

DISCUSSION

Nickel and cobalt films. From the two series of experiments it can be deduced that in the case of films evaporated in CO, olefins are chemisorbed easily to replace CO. However, CO does not disappear completely, in agreement with the fact that the adsorption energy increases as the surface coverage decreases (*3*). After this step CO cannot chemisorb again, but after treatment of hydrogen CO chemisorbs quickly. Even so, a very small amount of other species remains on the surface. In the case of films evaporated in H_2, CO chemisorbs easily, but after addition of olefins to a film freshly evaporated in H_2, CO cannot chemisorb even after treatment by hydrogen. Using the hypothesis put forward in the Introduction, it can be pro-

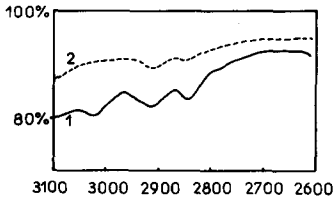


FIG. 3. Infrared spectra of chemisorbed propylene on Ni. Frequencies in cm^{-1}. (1) After introduction of propylene; (2) 3 hr after introduction of propylene.

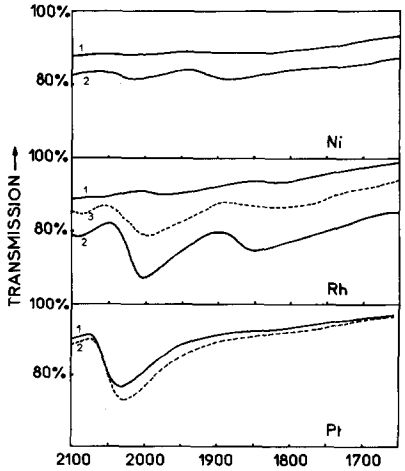


FIG. 4. Infrared spectra of chemisorbed CO on films evaporated under H_2. Frequencies in cm^{-1}. (1) After evaporation; (2) after addition of ethylene, H_2 and CO (3) after addition of ethylene and CO. In the case of Ni and Pt the spectra are identical to spectra 1.

posed that in the first case olefins produce surface species which are easily hydrogenated and replaced by CO; they may be monomers and low molecular weight polymers, with only a very small quantity of high polymers. In the second case, even if the surface species can be hydrogenated, they cannot be replaced by CO; they may be high polymers. In our observations CO appears to act as an inhibitor of high polymerization on nickel and cobalt films.

The mechanism of this inhibition of the polymerization in the presence of CO could be seen as a simple steric effect or as resulting from reactions between CO molecules and the olefinic species. For instance, Zakharov *et al.* (*11*) have proposed for the mechanism of the inhibition of the polymerization of olefins, an insertion reaction of the CO between the site and the polymeric chain.

In the case of chemisorption of ethylene, Blyholder and Goodsel (*12*) and Blyholder and Allen (*13*) have described an insertion reaction of CO to give an isopropoxide species.

An alternative explanation of our observations can be proposed. Preadsorbed hydrogen promotes the nondissociative form for chemisorbed olefins (*2*): this last form would polymerize easily, and hence hydrogen would appear to promote polymerization.

Experiments are now being performed to detect whether CO molecules react with chemisorbed olefins and to find other evidence in favor of the polymerization.

Rhodium and platinum films. Addition of olefins to films evaporated in CO produce a small shift of the CO stretching frequency to lower frequencies, and a small decrease of the intensity of the CO band. Addition of H_2 and then CO produces no change. Both observations are in agreement with a very limited chemisorption of olefins, to produce stable species.

The films evaporated in H_2 were partially covered with CO. After step 4, the CO surface coverage increases a little in the case of rhodium, and does not change in the case of platinum. The surface species produced by olefin chemisorption are stable in these conditions.

These experiments do not disagree with those performed on nickel and cobalt.

CONCLUSION

Olefins can easily remove CO from the surfaces of nickel and cobalt (but not from platinum and rhodium). When CO is lacking on the surface, it is postulated that chemisorbed olefins produce high polymers which shield the active sites, and the further chemisorption of CO is then impossible. From this point of view, CO seems to be a good inhibitor of polymerization on nickel and cobalt films.

REFERENCES

1. Anderson, J. R., and Baker, B. G., *in* "Chemisorption and Reaction on Metallic Films" (Anderson J. R., Ed.), Vol. 2. Academic Press, London, 1971.
2. Eischens, R. P., and Pliskin, W. A., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Eds). Vol. 10, Academic Press, New York, 1958.
3. Bond, G. C., *in* "Catalysis by Metals" Academic Press, London, 1962.
4. Frennet, A., Lienard, G., *J. Chim. Phys. Phys. Chim. Biol.* **67,** 598 (1970).
5. Soma, Y., *Bull. Chem. Soc. Jap.* **44,** 3233 (1971).
6. Sheppard, N., and Ward, J. W., *J. Catal.* **15,** 50 (1969).
7. Queau, R., and Poilblanc, R., *J. Catal.* **27,** 200 (1972).
8. Guerra, R. C., *J. Colloïd Interface Sci.* **29,** 229, (1969).
9. Queau, R., thesis, Toulouse, 1971.
10. Primet, M., Basset, J. M., Mathieu, M. W., and Prettre, M., *J. Catal.* **29,** 213, (1973).
11. Zakharov, V. A., Bukatov, G. D., Ermakov, Y. J., and Demin, E. A., *Dokl. Akad. Nauk. SSSR* **4,** 857, (1972).
12. Blyholder, G., and Goodsel, A. J., *J. Catal.* **23,** 374 (1971).
13. Blyholder, G., and Allen, M. C., *J. Colloïd Interface Sci.* **4,** 603 (1970).