JOURNAL OF CATALYSIS **110**, 18–22 (1988)

Coadsorption and Promoter Effects in the Adsorption of CO on Supported Rhodium Catalysts

P. A. J. M. ANGEVAARE, H. A. C. M. HENDRICKX,[1] AND V. PONEC[2]

Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Received October 21, 1986; revised July 10, 1987

The influence of benzene coadsorption and potassium promotion on the adsorption of CO on supported Rh catalysts has been studied using infrared spectroscopy. Benzene coadsorption and potassium promotion were found to lower the single coordinated CO singleton frequency by about the same amount (≈ 9 cm^{-1}). With potassium promotion a new peak with a singleton frequency of about 1795 cm^{-1} was found. It is concluded that benzene-induced redistribution of CO over the metal surface can explain the effects.

INTRODUCTION

In the Introduction of our preceding paper on Pd catalysts (*1*) reasons have been mentioned which made a study of coadsorption and promoter effects interesting from the point of view of catalysis. Before a general picture of these effects can be suggested it is necessary to collect data on several metals, and on identical pairs in the coadsorption and promoter–adsorbate interactions, as well as to gain information on various promoters or coadsorbates on one single metal. This paper extends our previous study, made with palladium, to rhodium.

EXPERIMENTAL

To facilitate comparison between earlier published results (*1, 2*) and the results of the present paper, all details of experimental work remain unchanged.

Two catalysts have been prepared, one with "small" and one with "large" particles. The first was prepared by homogeneous precipitation: a known amount of the support (Aerosil 150, Degussa), urea, and rhodium nitrate was mixed (pH ~3) and slowly heated upon stirring to 360 K. By hydrogenolysis of the urea the pH increases and rhodium hydroxide precipitates on the SiO_2 (pH ~8). After calcination at 380 K for several hours, reduction was performed at 500 K in a H_2 (25%)/N_2 stream. The large particle catalyst was prepared by impregnation and fast drying, followed by the same steps as those with the small particle catalyst.

Electron microscopy and X-ray line broadening showed that the catalysts had particles of approximately 2 and 6 nm, respectively. The large particle catalyst was used as a basis for preparing the promoted catalysts (the final state of the promoter being KOH/K_2O); these were prepared in the manner described in Ref. (*1*). The composition is designated by weight percent with respect to the amount of Rh. The promoted catalyst had Rh particles with $d \sim 6$ nm.

The IR spectroscopy, data gathering, and evaluation were the same as those in the earlier papers (*1, 2*). A monolayer CO coverage is defined by the state at 1 Torr (1 Torr = 133 Pa); coverages lower than unity are calculated from the integrated peak intensity I, with a linear relation being assumed to exist between I and θ. Benzene was adsorbed into the CO layer and by increasing the benzene pressure CO desorption resulted.

---

[1] Present address: Unilever Research Laboratories, P.O. Box 114, 3130 AC Vlaardingen, The Netherlands.

[2] To whom correspondence should be addressed.

0021-9517/88 $3.00

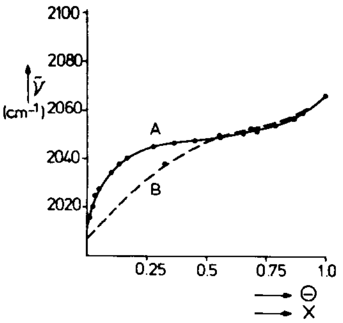

FIG. 1. Small particle Rh/SiO$_2$ catalysts. (A) Absorption maximum wavenumber of an adsorbed ^{12}CO layer at different surface coverages, θ(CO). (B) Absorption maximum wavenumber of a mixed ^{12}CO–^{13}CO layer at 1 Torr pressure. X is the molar ^{12}CO concentration in the adsorbed layer [X = ^{12}CO/(^{12}CO + ^{13}CO)] (1 Torr = 133 Pa).

RESULTS

The spectra of CO adsorbed on the Rh samples, as prepared in this study, are simple. The spectra at very low CO surface coverage are dominated by a band at 2012 cm^{-1} in the case of the small Rh particles, and at 2017 cm^{-1} with the large Rh particles. At high surface coverages, θ(CO) = 1, these bands appear at a considerably higher wavenumber, 2066 cm^{-1}. Next to the main band, which is ascribed to single coordinated (or "linear") CO, a small band is present at 1895 or 1870 cm^{-1}, for small and large particle rhodium catalyst, respectively. On our standard, well-reduced Rh sample no twin-CO absorption bands (due to Rh-dicarbonyls) are observed. This holds for the small as well as for the large particle size catalyst. However, the twin-CO absorption bands can appear in the spectra after precovering the Rh surface partially by oxygen.

Interesting phenomena are observed when the position of the main absorption band is studied as a function of either CO coverage (θ(CO)) or isotopic composition X [X = ^{12}CO/(^{12}CO + ^{13}CO)] at maximum surface coverage, θ(CO) = 1. The relevant data are presented in the Figs. 1 and 2. There are two remarkable features. First, the dipole–dipole interaction, that is the interaction which can be eliminated by isotopic dilution (*3–6*), is rather strong. Defining $\tilde{\nu}$ (at $\theta = 1$) $-$ $\tilde{\nu}$ (at $\theta = 0$) = $\Delta\tilde{\nu}$, we find $\Delta\tilde{\nu}$ = 60 and 55 cm^{-1} for small and large particles, respectively. This dipole–dipole interaction can therefore be regarded as responsible for the entire frequency variation with surface coverage, θ. Second, the two graphs, $\tilde{\nu}$ as a function of θ or X, do not coincide, but deviate from each other in a rather pronounced and well reproducible way. While the $\tilde{\nu}$ versus X curves do not differ too much for small and large particle rhodium catalysts, the $\tilde{\nu}$ versus θ curve on the small particle catalyst differs substantially from the $\tilde{\nu}$ as a function of X curve for this catalyst. Obviously, the effectively free sites on a small particle catalyst are distributed differently when they are created by either CO vacancies in the adsorbed layer (the case of the $\tilde{\nu}$ versus θ curve) or by ^{13}CO adsorption in a ^{12}CO layer ($\tilde{\nu}$ versus X). This last conclusion is based on the following consideration. The CO–CO interaction which leads to the increase in absorption frequency with increasing surface coverage, is a resonance interaction between two oscillating dipoles. Replacing a ^{12}CO by a ^{13}CO molecule has effectively almost the same consequences as removing a ^{12}CO molecule from a layer of adsorbed ^{12}CO molecules (*6–8*).

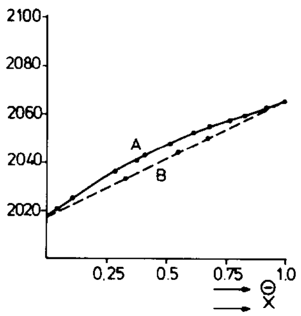

FIG. 2. Large particle Rh/SiO$_2$ catalyst. (A) Absorption maximum wavenumber of an adsorbed ^{12}CO layer at different surface coverage, θ(CO). (B) Absorption maximum wavenumber of a mixed ^{12}CO–^{13}CO layer at 1 Torr pressure. X is the molar ^{12}CO concentration in the adsorbed layer [X = ^{12}CO/(^{12}CO + ^{13}CO)].

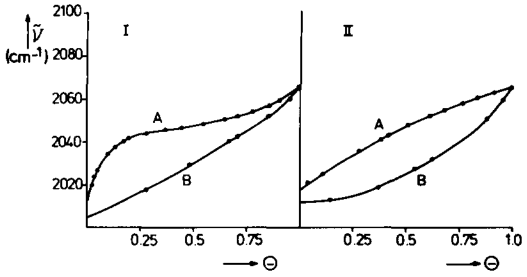

FIG. 3. Absorption maximum wavenumber of single coordinated ^{12}CO on a Rh/SiO_2 catalyst. (I) Small particle catalyst. (II) large particle catalyst. (A) CO admitted up to the indicated surface coverage $\theta(CO)$. (B) As (A), but benzene coadsorbed on the surface. $\theta(CO) = 1$, defined at 1 Torr CO.

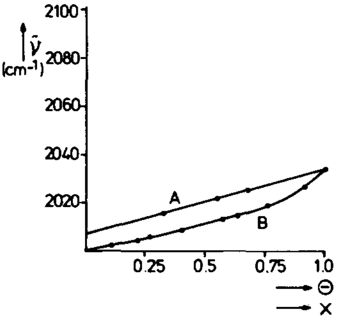

FIG. 5. Absorption frequency of single coordinated ^{12}CO on 45 wt% K with respect to Rh. (A) 1 Torr of CO admitted with X mol% ^{12}CO; (B) CO admitted up to the indicated surface coverage, θ.

The effect of coadsorbed benzene on the singleton frequency is rather small; there is a shift of about 8 cm^{-1} for small and 9 cm^{-1} for large rhodium particle catalysts. Benzene coadsorption influences the form of the $\tilde{\nu}$ versus θ curves, making them more monotonic. This is shown in Fig. 3.

Without going into detail but just by recalling the analogy with the conclusion made above with regard to Figs. 1 and 2, one can say that benzene most probably changes the distribution of CO molecules and free sites over the surface, making the distribution more homogeneous. An earlier paper on Pt (*9*) reports such effects as well.

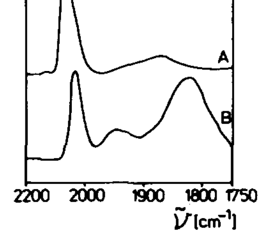

FIG. 4. IR spectra of the large particle Rh/SiO_2 catalyst. (A) No "potassium" deposited; (B) 45 wt% K with respect to Rh deposited.

Figure 4 shows the effects of K promotion on the spectra of adsorbed CO at $\theta(CO) = 1$, as observed with the large particle rhodium sample. Figures 5 and 6 show the variations with $\theta(CO)$ and X of the main and the new low frequency absorption bands, respectively. Both figures were obtained with the large particle sample. It should be noted that as far as the main CO band is concerned, the "linear CO" singleton (i.e., at $\theta(CO) = 0$) frequency is only 5–10 cm^{-1} lower than that obtained with the unpromoted Rh sample. The main effect of the promoters on this band is at $\theta(CO) = 1$ (compare the Figs. 2 and 5, at $\theta(CO) = 1$), where it amounts to about 30 cm^{-1}. Obviously, the main effect of the potassium promoter on this high frequency CO band is dilution of the CO layer which is suppressing the CO–CO interactions. Either the low frequency band can be a band created by a very large shift of another band (e.g., of the multicoordinated CO with an absorption at about 1870 cm^{-1}) or it is a newly formed band, present only on the promoted samples. However, it is improbable that the K promoter would shift the singleton wavenumbers by 5–10 cm^{-1} with single coordinated CO, but at least 70 cm^{-1} with the multiply coordinated CO. Thus the second explanation is more likely. It is interesting to see that this new low frequency band shows a pronounced nonlinear behavior with respect to $\theta(CO)$, similar to that of the analogous band observed with Pd (*1*). Furthermore, it is worthwhile mentioning that

TABLE 1

Maximum Dipole–Dipole Interaction Effect

Metal	Form	$\Delta\tilde{\nu}$ (cm^{-1})	Ref.
Pt(111)	Single crystal	36	*3*
Pt	Powder	40	*6, 20*
Ir	Evaporated film	50	*5*
Ir	Powder	52	*15, 16*
Pd(100)	Single crystal	35	*18, 19*
Pd	Powders	21–28	*2*
Rh	Powders	55–60	This paper
Cu	Single crystal	36	*21*
Cu	Powder	~38	*6*

the deviation between the $\tilde{\nu}$ versus X and $\tilde{\nu}$ versus θ(CO) curves is just opposite to that found on the unpromoted surfaces.

DISCUSSION

That the maximum effect of the dipole–dipole interactions, $\tilde{\nu}_{\max} - \tilde{\nu}_{\min} = \Delta\tilde{\nu}$, as established by isotopic dilution experiments, is different for different metals deserves attention. This can be seen in Table 1. There is no definitive explanation of this observation, but it confirms the conclusion in the literature (*10–14*) that at least a part of the dipole–dipole interactions is mediated by the metal. With Pd powders or Pt (and to a great extent with Ir, too) the $\tilde{\nu}$ versus θ and $\tilde{\nu}$ versus X curves almost coincide. They do not do so when CO is allowed to precipitate into clusters (*3, 4, 17*) or when CO can switch among several adsorption sites such as occurs in particular on smooth single crystal faces (*2, 18, 19*). Rhodium is one of the metals where the two curves, $\tilde{\nu}$ versus θ and $\tilde{\nu}$ versus X, do not coincide either. The large difference between the $\tilde{\nu}$ versus θ and the $\tilde{\nu}$ versus X curves on rough surfaces of small particles becomes smaller when benzene is coadsorbed or when a large particle sample is used instead of the small particle rhodium sample (see Fig. 3). Since the singleton frequency (that is the frequency which should reveal pure "ligand" or "electronic structure" effects) does not differ in a pronounced way, one can speculate that the main influence of benzene coadsorption (or of smoothing the surface by making particles larger) on the shape of the $\tilde{\nu}$ versus θ curves is through the redistribution of CO over the surface. This tentative conclusion is supported by the results obtained with the potassium-promoted rhodium surfaces (see Figs. 5 and 6).

Here the $\tilde{\nu}$ versus X and $\tilde{\nu}$ versus θ curves differ in just the opposite sense and the most plausible explanation is that the potassium promoter causes clustering of CO round the centers (K^+) which adsorb CO in a form having a lower vibration frequency. The same holds then for the high frequency (single coordinated or "linear" CO) as well as for the new (appearing only on promoted surfaces) low frequency band. A recent model (*24*) is in full compliance with our data.

Our previous paper on Pd (*1*) reported that the effect of benzene coadsorption was (with Pd) particle size dependent. It has been concluded that either the size of a "ligand" effect is particle size dependent or benzene causes a redistribution of CO which is more "felt" with small than with large particles. The data obtained with Rh (in this paper) point in the direction of the second explanation. Redistribution of CO among different sites by benzene coadsorption is moreover a fact well established by

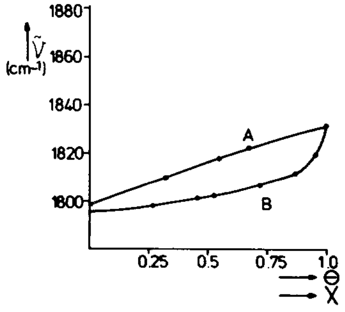

FIG. 6. Absorption frequency of the newly formed adsorption state on the potassium-promoted Rh/SiO$_2$ catalyst. (A) 1 Torr of CO admitted with X mol% ^{12}CO; (B) ^{12}CO admitted up to the indicated surface coverage θ.

LEED data analysis (*22, 23*). Thus, although the conclusion cannot be made definitive yet and the particle-size-dependent ligand effects of coadsorption should still be considered, new information seems to favor the explanation by CO redistribution.

ACKNOWLEDGMENT

The financial support by SON/ZWO-Netherland, EEC Science Committee, and by NATO are acknowledged.

REFERENCES

1. Angevaare, P. A. J. M., Hendrickx, H. A. C. M., and Ponec, V., *J. Catal.* **110,** 11 (1988).
2. Hendrickx, H. A. C. M., des Bouvrie, C., and Ponec, V., *J. Catal.* **109,** 120 (1988).
3. Crossley, A., and King, D. A., *Surf. Sci.* **68,** 528 (1977).
4. Crossley, A., and King, D. A., *Surf. Sci.* **95,** 31 (1980).
5. Reinalda, D., and Ponec, V., *Surf. Sci.* **91,** 113 (1979).
6. Toolenaar, F. J. C. M., van der Poort, G. J., Stoop, F., and Ponec, V., *J. Chim. Phys.* **78,** 927 (1981).
7. Decius, J. C., *J. Chem. Phys.* **23,** 1290 (1955).
8. Hammaker, R. M., Francis, S. A., and Eischens, R. P., *Spectrochim. Acta* **21** 1295 (1965).
9. Stoop, F., Toolenaar, F. J. C. M., and Ponec, V., *J. Catal.* **73,** 50 (1982).
10. Persson, B. N. J., and Ryberg, R., *Phys. Rev. B.* **24,** 6954 (1981).
11. Persson, B. N. J., and Liebsch, A., *Surf. Sci.* **110,** 356 (1981).
12. Ryberg, R., *Surf. Sci.* **114,** 627 (1982).
13. Persson, B. N. J., and Persson, M., *Solid State Commun.* **36,** 175 (1980).
14. Hellsing, B., Persson, M., and Lundquist, B. I., *Surf. Sci.* **126,** 147 (1983).
15. Reinalda, D., Ph.D. thesis, Leiden University, The Netherlands, 1979.
16. Toolenaar, F. J. C. M., Bastein, A. G. T. M., and Ponec, V., *J. Catal.* **82,** 25(1983).
17. Shigeishi, R. A., and King, D. A., *Surf. Sci.* **58,** 379 (1976).
18. Ortega, A., Hoffmann, F. M., and Bradshaw, A. M., *Surf. Sci.* **119,** 79 (1982).
19. Ortega, A., Ph.D. thesis, Berlin, Germany, 1980.
20. Heyne, H., and Tompkins, F. C., *Trans. Farad. Soc.* **63,** 1274 (1967).
21. Hollins, P., and Pritchard, J., *Surf. Sci.* **89,** 486 (1979).
22. Koel, B. E., Crowell, J. E., Mate, C. M., and Somorjai, G. A., *J. Phys. Chem.* **88,** 1988 (1984).
23. van Hove, M. A., Lin, R. F., and Somorjai, G. A., *Phys. Rev. Lett.* **51,** 778 (1983).
24. Uram, K. J., Ng, L., Folman, M., and Yates, J. T., Jr., *J. Chem. Phys.* **84,** 2891 (1986), and references therein.