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Coadsorption and Promoter Effect in the Adsorption of CO on Palladium Catalysts

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Infrared spectroscopy has been used to study the influence of C_6H_6 coadsorption and potassium compound promotion on the adsorption of CO on supported Pd catalysts. Benzene is found to have a significant influence on single coordinated CO provided small Pd particles are being used. The promotion by potassium compounds has little influence on the single coordinated CO, but one finds on promoted Pd a new peak with a singleton frequency of about 1740 cm^{-1}. The possible nature of this peak is discussed. © 1988 Academic Press, Inc.

INTRODUCTION

Two aspects of catalytic reactions which have recently attracted much attention from surface scientists are coadsorption from gas mixtures and the function of promoters. This is no coincidence, since catalytic reactions usually take place in gas mixtures (coadsorption) and almost all catalysts used in practice are multicomponent solids. In the simplest case a multicomponent catalyst consists of an active component (e.g., a metal) and a support. It is not very exceptional that in such a case some of the support material appears on the surface of the active component and plays there a role comparable to that of a more traditional promoter (e.g., "potassium").

The question as to what extent the adsorption of one gas is influenced by the adsorption of another is of a fundamental nature. Early papers which studied the problem by IR spectroscopy on CO adsorption reported very pronounced effects on the absorption frequency of CO when this gas was adsorbed on a surface partly covered by, e.g., hydrocarbons, or by other molecules (*1–8*). Later it appeared that a substantial part of the total effect (over 60%) was, on Pt at least, actually caused by the rather trivial and well-known suppression of the CO–CO response interaction in the mixed surface layer (*9*).

A reexamination of the problem under conditions when a low CO–CO interaction could be assumed revealed that on Pt a coadsorption of CO with benzene, ethylene, ammonia or oxygen can cause a quite significant adsorption frequency shift ($\Delta\nu$ = 43, 37, 67, and −15 cm^{-1}, respectively) (*10*). There is therefore the problem that different groups are using different experiments, studying the same interaction on almost identical catalysts and they come to very different conclusions. Up to now no ideas to explain this discrepancy have been suggested. An extension of the coadsorption experiments to another metal could be a way to confirm a general character of one of the conclusions mentioned.

Among the various promoters used with metallic catalyst, alkali compounds are probably easiest to study. Earlier research has already provided extensive information on CO adsorption in the presence of alkali metals (*8, 11–31*). Remarkable features of this "coadsorption" are:

(1) a downward shift in the CO vibration frequencies;

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(2) an influence of the promoter on the ratios in population of the various (differently coordinated) CO molecules; and

(3) the appearance of a new band (or bands) in the very low frequency region.

These points are illustrated in Table 1.

TABLE 1

Effect of Coadsorbed Metals on the Frequency (cm^{-1}) of Absorption of CO Adsorbed on Different Metals

Metal	Coads	θ(coads)	θ(CO)	ν(CO) (cm^{-1})	Ref.
Rh(111)	—	0	0.05	2016	*30*
	—	0	1	2065	*30*
	—	0	1	1855	*30*
	K	0.1	0.9	2030	*30*
	K	0.1	0.9	1805	*30*
	K	0.25	0.75	2000	*30*
	K	0.25	0.75	1710	*30*
Pt(111)	—	0	1	2120	*14*
	—	0	1	1870	*14*
	K	0.1	0.9	2055	*14*
	K	0.1	0.9	1775	*14*
	K	0.3	0.7	2000	*14*
	K	0.3	0.7	1725	*14*
	K	0.3	0	1400	*14*
	K	0.6	0.4	1565	*14*
Cu(110)	—	0	1	2090	*22*
	K	0.2	0.8	2090	*22*
	K	0.2	0.8	1490	*22*
	K	~1	~0	1575	*22*
	K	~1	~0	1220	*22*
Ir(film)	K	~0	~1	2072	*8*
	K	~1	~0	2028	*8*

Note. Variations in θ(CO) and θ(coadsorbate) indicated.

It can be expected that alkali metals, when adsorbed on a metal, bear a positive charge, δ^+, making them indicative of alkali ions. Therefore, effects similar to those shown in Table 1 can be expected when CO is adsorbed on a metal surface modified by either a layer of an alkali metal or an alkali compound. Indeed, Ni/SiO_2 catalysts promoted by K compounds show effects similar to those of metal surfaces promoted by alkali metals (*32*).

EXPERIMENTAL

Two palladium-on-silica catalysts have been prepared, one with a small (≃5.0 nm) and one with a large (≃16.5 nm) particle size, with a silica support (Aerosil 150). First, silica was very well suspended in water, the temperature was fixed at 350 K, and the pH was fixed at 8–9. Then, an aqueous solution of $Pd(NH_3)_4(NO_3)_2$ was slowly added under continuous stirring whereupon adsorption on the silica occurred. The concentration of Pd nitrate was such that at complete adsorption (almost achieved) the loading by Pd was 10 wt% Pd. After some time the suspension was filtered and the powder dried overnight in air at 370 K. The catalyst was prepared free of Cl ions. The reduction took place in 25% H_2/75% N_2 mixture, the temperature being slowly raised to 600 K and maintained at this value for several hours. The large particle catalysts were prepared by direct impregnation and fast evaporation of the liquid at 370 K.

The fresh Pd catalysts showed the usual pattern upon CO adsorption: there was the more pronounced low frequency peak(s) (multicoordinated CO) and the high frequency (linear, on top adsorption mode) absorption. However, by repeated CO adsorptions following a cleaning by evacuation, oxidation, and rereduction, a steady state of the catalysts is reached in which they reveal a more pronounced high frequency CO IR absorption. In this paper only data for the steady-state catalysts are presented.

Promoted catalysts were prepared by impregnating the reduced and passivated catalyst of a given particle size by a solution (of required concentration) of KNO_3. The liquid was evaporated from the slurry by drying under stirring at 373 K. Afterward, the standard reduction (see above) *in situ* was performed at 600 K. Under the conditions of preparation KNO_3 is expected to be converted into K_2O and KOH (*33*). It is very improbable that the reduction proceeds any further (*33, 34*). With hydrogen atoms, reduction to metallic potassium is in principle possible when the H_2O pressure is low enough. However, it is improbable that such low water pressures are achieved with powder samples containing silica (*35, 36*). For the sake of simplicity the catalysts containing the potassium compound(s) are called "potassium-promoted" catalysts.

Potassium promotion did not change the Pd particle size of the "small particle" Pd catalyst. Catalysts with varying amounts of potassium promoter (2, 10, and 45 wt% with respect to Pd), all originating from the 5.0-nm Pd catalyst, show after promotion particles of 5.0 + 0.5 nm. The large particle Pd catalyst was not changed (≃17.0 nm) either. There are no data on the distribution of the potassium promoter over the metal and the support surfaces. However, it can be inferred from the data that the potassium promoter is for a substantial part covering the metal, since even small potassium promoter concentrations (2 wt% K with respect to Pd) have a marked influence on the CO IR absorption spectrum.

When the coadsorption of benzene and CO was studied, the amount of benzene needed was evaporated from a 99.98+% purity liquid benzene into the vacuum system. The maximum partial benzene pressures used were about 40 Torr. The procedure of CO/benzene coadsorption measurements was as follows. The given sample was first covered by CO. The state achieved at $p(\mathrm{CO}) = 1$ Torr is defined as the "monolayer" coverage by CO. The CO IR absorption peak area has been calculated and used as a measure of the coverages by CO of the surface with benzene coadsorbed thereon. With this determination a proportionality absorption peak area coverage (θ) has been assumed and only the high frequency absorption of the low coordinated CO considered. Various $\theta(\mathrm{CO})$ coverages were achieved by admitting an increasing amount of benzene into the cell and desorbing CO by displacement.

The IR cell and the gas-handling system were of conventional design. The spectra of the catalysts, obtained using self-supporting pellets, were recorded with a Perkin–Elmer 580B spectrophotometer operating in the transmission mode. Data collection, storage, and handling were performed with on-line connected Apple II+ computer system. The recorded spectra were converted into "change in extinction" versus "frequency" plots, before being interpreted; for this calculation the spectrum of a freshly reduced, evacuated, and CO-free catalyst was used as background. More experimental details can be found in Refs. (*37, 38*).

RESULTS

The IR spectra, obtained with Pd/SiO_2 samples bearing CO adsorbed at 1 Torr pressure, show the well-known features of CO adsorption by Pd powder catalysts; there is a sharp band at about 2080 cm^{-1} and a broad double band, with a maximum near 1905 cm^{-1} and a shoulder at 1960 cm^{-1} (*39–42*). As already mentioned above, a fresh catalyst with small particle size shows more pronounced 1960 and 1905 cm^{-1} absorption bands than the same sample aged by repeated CO oxidation and hydrogen reduction cycles or a sample with large metal particles. In contrast to earlier results obtained with Pt and Ir powders (*43*), the fresh, small and large particle catalysts do not differ substantially in the position of their single coordinated CO band (2080 cm^{-1} at $\theta(\mathrm{CO}) = 1$). There is also no broadening with diminishing particle size of the sharp, high frequency band, such as is observed with Ir (*43*).

To facilitate comparison, in Fig. 1 there are two plots in the same diagram. The plots are:

(1) the wavenumber of the band maximum of adsorbed $^{12}\mathrm{CO}$ versus the surface coverage, θ, where θ is defined as being unity after admission of 1 Torr CO into the gas phase (1 Torr = 133 Pa);

(2) the wavenumber of the symmetric layer vibration (characteristic of $^{12}\mathrm{CO}$ adsorption) versus X, X being the fraction of the $^{12}\mathrm{CO}$ molar concentration [$X = {}^{12}\mathrm{CO}/({}^{12}\mathrm{CO} + {}^{13}\mathrm{CO})$] in a $^{12}\mathrm{CO}$–$^{13}\mathrm{CO}$ mixture.

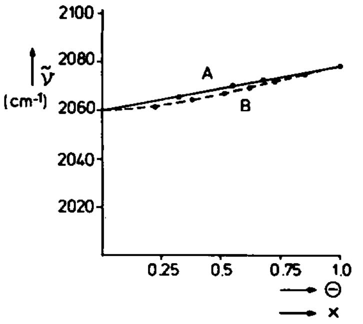

FIG. 1. Small particle Pd/SiO$_2$ Catalyst. Full line, IR absorption wavenumber of a mixed ^{12}CO–^{13}CO layer at 1 Torr pressure. X is the molar ^{12}CO fraction in the adsorbed layer = ^{12}CO/(^{12}CO + ^{13}CO). Dashed line; IR absorption wavenumber of adsorbed ^{12}CO at different surface coverages, θ(CO). (1 Torr = 133 Pa.) Both X and θ are on the same axis, scaled from zero to unity.

A good coincidence of these two graphs, as can be seen in Fig. 1, indicates that under our experimental conditions there are no problems caused by the possible clustering of adsorbed CO molecules. It has been pointed out earlier that clustering of the CO molecules upon adsorption causes the two functions plotted in Fig. 1 to deviate from each other (*44–47*), the $\tilde{\nu}(\theta)$ curve being steeper at θ(CO) = 0 (and X = 0), than $\tilde{\nu}$ (X).

Figure 2 shows the influence of benzene coadsorption on the position of the high frequency CO band. When the small particle Pd sample is used, the effect of coadsorption is pronounced, in particular at low θ(CO). However, when the same phenomena are studied in exactly the same way, but with the large particle catalyst, the effect of coadsorption is very limited. This is shown in Fig. 3.

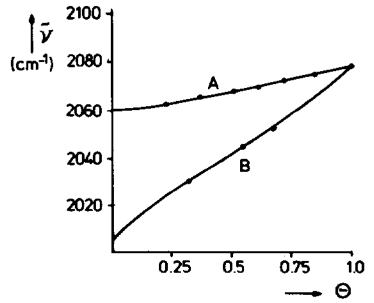

FIG. 2. Small particle Pd/SiO$_2$ catalyst. (A) Wavenumber of adsorbed ^{12}CO at different surface coverages, θ(CO). (B) Wavenumber of adsorbed ^{12}CO at different CO surface coverages, θ(CO), with benzene coadsorbed on the surface.

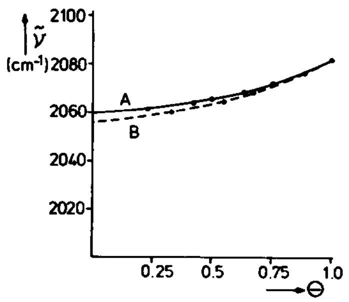

FIG. 3. Large particle Pd/SiO$_2$ catalyst. (A) Wavenumber of adsorbed ^{12}CO at different surface coverages, θ(CO). (B) Wavenumber of adsorbed ^{12}CO at different CO coverages, θ(CO), with benzene coadsorbed on the surface.

Figure 4 shows the effect of "K" promotion on the CO/IR spectra. The spectra shown were recorded after admitting 1 Torr of CO to the catalyst.

Figure 5 presents the data on the position of the newly formed absorption peak which

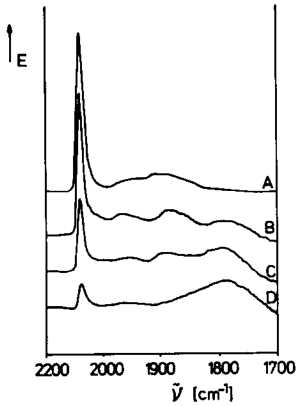

FIG. 4. IF spectra of promoted small particle Pd/SiO$_2$ catalysts. (A) No potassium deposited, magnification = 1; (B) 2 wt% K with respect to Pd, magnification = 1.5; (C) 10 wt% K with respect to Pd, magnification = 2; (D) 45 wt% K with respect to Pd, magnification = 2. All spectra were taken at 1 Torr ^{12}CO pressure.

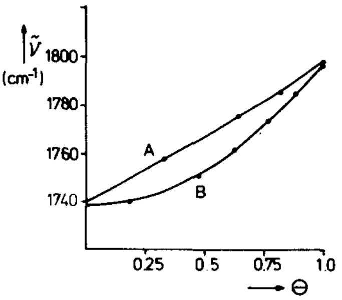

FIG. 5. Small particle K-promoted Pd/SiO$_2$ catalysts. IR absorption wavenumber of the newly formed adsorption state, at different CO surface coverages, θ(CO). (A) 10 wt% K with respect to Pd; (B) 2 wt% K with respect to Pd.

appears after CO admission to a K promoted Pd catalyst. The other absorption peaks present in the spectrum do not show a shift that exceeds the measurement error, neither do they show a diminished dipole–dipole interaction, as already mentioned. When CO molecules, adsorbed on a metal surface, tend to form clusters, this can be detected by comparing the wavenumber of the band maximum versus θ(CO) curve with the wavenumber of the band maximum versus molar fraction ^{12}CO, X (at θ(CO) = 1) plot. Since the CO–CO interaction leading to an increase in the frequency is a resonance effect, the replacement of ^{12}CO by ^{13}CO simulates the creation of a free site. For more details, see Refs. (*48, 49*).

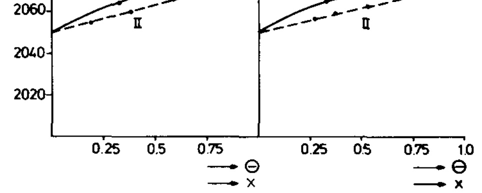

FIG. 6. Absorption wavenumber of single coordinated ^{12}CO on (45 wt% K with respect to Pd) promoted catalyst. (I) 1 Torr of CO admitted with X mol% ^{12}CO. (II) CO admitted up to the surface coverage, θ(CO). (A) Large particle catalyst; (B) small particle catalyst.

The two graphs mentioned ($\tilde{\nu} = f(\theta)$; $\tilde{\nu} = f(X)$) are compared in Fig. 6 for two samples differing in their particle size. The variations in the position of the frequency CO band (single coordination) are shown.

DISCUSSION

The fact that CO adsorbed on Pd shows a little tendency toward clustering (see Fig. 1) on both large and small particles supports the conclusion reached by Primet (*10*) on Pt that the effects of coadsorption he observed were probably not caused by a "trivial" clustering. The effect of benzene coadsorption is very much dependent on the particle size of the Pd metal. It is only pronounced (see also Ref. (*10*)) with small particles. There can be two possible explanations for this fact:

(1) The effect observed is a real "ligand" effect of the coadsorbed benzene on the adsorbed CO, and this effect is particle size dependent, being smaller on large particles.

(2) The ligand effect of coadsorbed benzene with small particles is as small as it is with the large ones (about 5 cm^{-1}), but on small particles this effect is superimposed by another effect, namely changes in the position of coadsorbed CO induced by benzene or by its fragments formed upon adsorption.

Shifts in the position of CO molecules on the surface due to benzene coadsorption are known to occur with Rh and Pt (*10, 13*), but it is not clear why they should be more pronounced on small than on large particles. Nor is it clear why the localized effect mentioned in (1) above should be particle size dependent. For the moment one must keep in mind both effects as possible interpretations.

The next point to be discussed is the influence of the K promoter on the behavior of adsorbed CO. The most pronounced feature here is the appearance of the new band at low frequencies. As can be seen in Table 2, the position of this new band is at higher wavenumbers than those observed with

TABLE 2

Effect of Promoters on the Frequency (cm^{-1}) of Absorption in the Region of Lowest Frequencies

Metal	Promoter	Absorption frequency new band (cm^{-1})	Ref.
Ru(001)	K	1460	*12, 15*
Ru(001)	K	~1490	*23*
Ru(001)	K	~1600	*23*
Cu(110)	K	1220	*22*
Cu(110)	K	1575	*22*
Cu(100)	Na	~1360	*50*
Fe(111)	K	~1400	*26*
Fe(111)	K	~1550	*26*
Pt(111)	K	>1400	*14, 17*
Rh(111)	K	>1530	*30*
Ni/SiO_2 powder	K_2O, KOH ex. KNO_3	~1780	*32*

Note. Systems in which formation of a new (indicated) band can be suspected.

metallic potassium or sodium as promoter. However, with regard to the unpromoted surface, the change is still considerable. The most likely assignment of this band is that it reflects a local CO–K^+ interaction, which changes the CO behavior in a very pronounced way. However, this must be a type of interaction that can be influenced by an increasing surface coverage of CO (see Fig. 5). For example, CO forms strongly influenced clusters round K^+ and it is adsorbed on the rest of the surface with much less perturbation. Actually, such models have already been suggested in the literature (*51*) and they are also applicable here. The fact that the $\tilde{\nu}$ versus X curve ($f(X)$) is more steep at low θ(CO) (and X) than the $\tilde{\nu}$ versus θ curve ($f(\theta)$) indicates indeed that there is a small and not very pronounced tendency of CO to cluster. This clustering probably takes place around K^+ or around the CO–K^+ complexes. This effect is even more clearly seen with Rh as adsorbent than with palladium (*52*).

It is worthwhile mentioning that the presence of a K promoter on the Pd surfaces does influence the singleton frequency of the single coordinated CO only in a rather limited way (at most about 10 cm^{-1}). It is important to take this value into account before starting to speculate on the ligand effects of coadsorption and/or promotion by potassium compounds.

Note added in proof. "Ligand" effect comprises all effects other than "geometrical" ones; includes thus also the "electrostatic" field effects.

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