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Infrared Spectroscopic Study of the Interaction between Carbon Monoxide and Hydrogen on Supported Palladium

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Preadsorbed carbon monoxide on alumina-supported palladium can be used as an indicator to examine the rearrangement of the metallic surface upon the action of hydrogen. The changes of the ir spectra from CO on Pd/Al_2O_3 when the sample is brought into contact with hydrogen show that the Pd(111) plane is formed on disordered palladium crystallites even at room temperature, probably as a result of the formation of palladium hydride. Depending on the experimental conditions a number of ir bands are observed when a mixture of CO and H_2 is passed over the catalyst. These bands are believed to belong to intermediates of carbon monoxide hydrogenation. It is suggested that the surface species is formed *on* palladium and after that is strongly adsorbed on alumina due to the spillover phenomenon. An attempt is made to explain the difference between the reaction pathways of methanation and methanol formation.

INTRODUCTION

Infrared spectroscopy in its transmission mode has been extensively applied to investigations of carbon monoxide adsorption on supported metals, especially on palladium (*1–9*). The distinction suggested by Eischens and Pliskin (*1*) between linear and bridged CO groups is confirmed in all of the cited papers. A much more thorough interpretation, however, of the ir spectrum from CO adsorbed on supported palladium became possible after the development of new physical techniques, especially ir reflection–absorption spectroscopy (*10–13*).

Infrared data on carbon monoxide and hydrogen coadsorption on alumina-supported palladium showed interesting phenomena concerning the adsorbate effect on the adsorbent structure and also enabled us to verify the ir band assignments made earlier for CO adsorbed on Pd/Al_2O_3 to be checked (*9*). The interaction between carbon monoxide and hydrogen has received much attention in connection with the catalytic synthesis of organic materials. Although palladium is not among the most active Group VIII metals for carbon monoxide hydrogenation, data obtained with this metal provided a new insight into the chemistry of the CO–H_2 reaction catalyzed by metallic surfaces. Moreover, Vannice and Garten (*14*) recently reported high methanation activity for Pd/Al_2O_3 catalysts which was comparable to that of typical nickel methanation catalysts.

Infrared Spectra of Carbon Monoxide Adsorbed on Palladium

For better understanding of the results to be discussed in the present paper, an attempt will be made to summarize briefly current data concerning the assignment of the ir bands from CO adsorbed on palladium. Recently, Hoffmann and Bradshaw developed a combined LEED and reflection infrared system which enabled them to obtain good-quality spectra of CO adsorbed on various single-crystal faces (*10–13*). Using data obtained with this technique, a link can be realized between single-crystal studies and those of supported metals, and thus more precise interpretation of the spectrum of carbon monoxide adsorbed on alumina-supported palladium may be given.

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At low coverages the room-temperature adsorption of CO on Pd/Al_2O_3 catalysts gives rise to only one band at about 1920 cm^{-1}, most probably due to the higher concentration of adsorbed molecules on the outer edge of the disk compared to the interior part, i.e., the so-called "hit-and-stick" effect (*8*, *9*). However, during thermal desorption, two well-resolved bands appear at 1820 and 1900 cm^{-1} for surface coverage decrease from 1 to 0.3 (Fig. 1a). The latter two bands can also be observed if a portion of CO is added to a reduced sample at about 200°C to obtain surface coverage less than 0.3. Under these conditions, appropriate coverage and temperature, the adsorbed CO molecules becomes more mobile and order on the surface as hardly-interacting three- and two-centre-bonded species (*9*). Enhanced interaction, however, does occur at increasing surface coverage as deduced from the CO band displacement (*8*, *9*, *13*). The shift of the CO bands to higher frequencies is explained as originating from dipole–dipole coupling and interaction via the metal (*13*). Elevated temperatures cause higher rates of CO diffusion in the catalyst disk thus eliminating the hit-and-stick effect. It should be emphasized that CO dissociation on palladium does not take place to a significant extent at a temperature below 200°C as observed by specially performed experiments (*8*). Investigations of the CO adsorption on palladium by various physical techniques also show that this adsorption appears to be predominantly molecular (*15*).

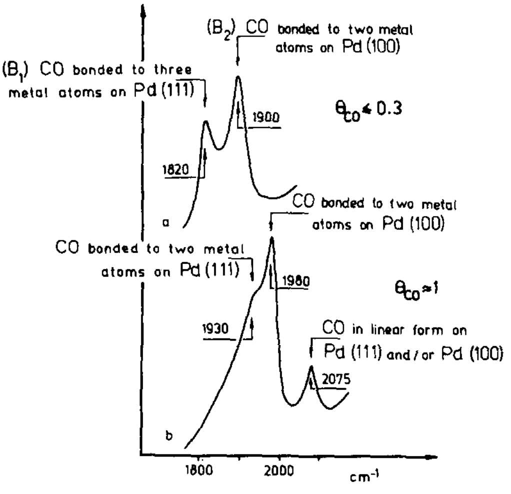


FIG. 1. Infrared spectra of carbon monoxide adsorbed on a Pd/Al_2O_3 sample of low dispersion and their interpretation according to Refs. (*9–13*): (a) at low surface coverage ($\theta_{CO} \approx 0.3$); (b) at high surface coverage ($\theta_{CO} \approx 1$).

In a reflection–absorption study Bradshaw and Hoffmann (*13*) observed a band at 1823 cm^{-1} for the CO/Pd(111) system at $\theta = 0.06$. At increasing coverage this band is shifted continuously from 1823 to 1946 cm^{-1} at $P_{CO} = 1 \times 10^{-5}$ Torr (1 Torr = 133.3 N m^{-2}). The same authors have reported that the band at 1900 cm^{-1} due to CO adsorbed on the Pd(100) plane is shifted to 1980 cm^{-1} at higher CO pressures (*10*). The bands at 1820 and 1900 cm^{-1} from CO adsorbed on Pd/Al_2O_3 (Fig. 1a) are also shifted at increasing coverage to reach 1930 and 1980 cm^{-1}, respectively (*9*) (Fig. 1b). At higher CO coverages bands above 2000 cm^{-1} appear on both supported Pd (*9*) and Pd single crystals (*13*). The assignment of the bands shown in Fig. 1 was made on the basis of data reported in Refs. (*9–13*). This assignment is somewhat different from the interpretation given earlier (*9*), since ir reflection–absorption data on CO adsorbed on the Pd(111) plane appeared after our paper (*9*) was submitted for publication. Recently Sheppard and Nguyen (*16*), in an excellent review on the vibrational spectra of CO adsorbed on metals, suggested a scheme of interpretation of the ir spectra from CO adsorbed on palladium which is in agreement with the assignments made above.

EXPERIMENTAL

Catalysts were prepared by impregnating alumina or silica (Degussa) with $PdCl_2$ solution sufficient to yield nominal 9% of palladium. The powder was dried at 60°C and pressed (3 t/cm^2) into self-supporting disks which weighed about 130 mg (20 × 15 mm).

Oxygen treatment (P_{O_2} = 10 Torr) was carried out at 300°C for 10 min. After brief evacuation the samples were reduced in a stream of hydrogen at the same temperature for 5 h. The cell was finally evacuated at 320°C down to 1×10^{-5} Torr. Catalysts were reactivated by oxidation, degassing, re-reduction by hydrogen at 300°C for 20–30 min, and evacuation to remove adsorbed hydrogen.

Since the palladium concentration was too high, the catalyst dispersion was low (*9*). Metal particle sizes, 8 and 12 nm on alumina and silica, respectively, were determined by hydrogen chemisorption, following Aben's procedure (*17*).

Carbon monoxide, "puriss" grade (Fluka), was used without further purification. Hydrogen gas was passed through a Deoxo unit and a liquid nitrogen trap before use.

All experiments were carried out with a conventional vacuum device equipped with a circulating pump, calibrated volumes, and an infrared cell with two sections for the sample holder (*18*).

Infrared spectra were recorded in the absorbance mode on a double-beam UR-10 spectrometer, applying slitwidth and scanning rates so as to give minimal noise in the baseline. Spectra were taken by placing an optical attenuator in the reference beam.

RESULTS

(*a*) *Carbon Monoxide and Hydrogen Coadsorption on Pd/Al_2O_3 under Static Conditions*

In Fig. 2a the room-temperature spectrum of carbon monoxide adsorbed on Pd/Al_2O_3 at surface coverage $\theta = 0.2$ is shown. It was significantly affected by successive additions of hydrogen and changes depended on hydrogen pressure and contact time (Figs. 2b–e). In general, the effect of coadsorbed hydrogen on the ir spectrum from preadsorbed carbon monoxide was manifested in three ways: (i) change of band position (Figs. 2a–c); (ii) appearance of new bands and change of the relative intensities (Figs. 2b–d); (iii) decrease in intensity of all the bands with increasing contact time between preadsorbed carbon monoxide and hydrogen (Fig. 2e). It is worth noting that initial intensities were restored upon hydrogen evacuation (Fig. 2f).

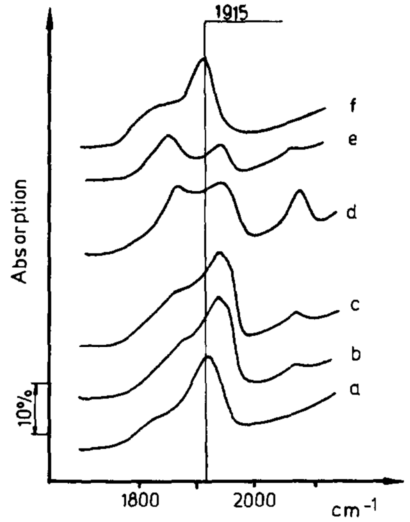


FIG. 2. Infrared spectra of CO adsorbed on Pd/Al_2O_3 after hydrogen coadsorption: (a) CO adsorbed at 35°C; θ_{CO} = 0.2; (b) to (d), hydrogen added after (a) at pressures of: (b) 1 Torr; (c) 11 Torr; (d) 700 Torr; (e) 18 h after (d); (f) evacuation down to 1×10^{-5} Torr.

As is seen in Fig. 1a two bands are observed in the ir spectrum from carbon monoxide adsorbed on Pd/Al_2O_3 under certain experimental conditions (see Introduction). In this case the effect of hydrogen on the ir spectrum of carbon monoxide adsorbed on Pd(111) and Pd(100) can be detected separately. The changes induced by successive hydrogen additions are presented in Fig. 3. At increasing hydrogen equilibrium pressure from 1×10^{-5} to 1×10^{-2} Torr the bands shifted to 1850 and 1920 cm^{-1}, respectively (Fig. 3c). Further increase of hydrogen pressure caused not only displacement but also altered the relative intensities of the two peaks (Figs. 3d–f). A band above 2000 cm^{-1} also appeared and increased in intensity with the increase in hydrogen pressure (Figs. 3d–f). The position of this

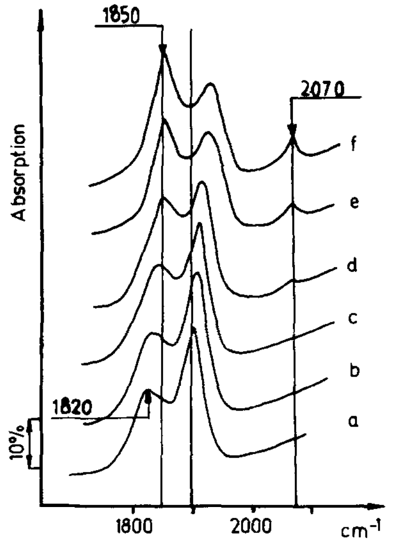


FIG. 3. Effect of hydrogen coadsorption on the bands assigned to CO adsorbed on the Pd(111) and Pd(100) faces of a Pd/Al_2O_3 sample: (a) CO added (θ_{CO} = 0.2) and the sample is annealed in a closed cell at 200°C for 10 min; the spectrum is taken at 35°C; (b) to (f), hydrogen added after (a) at pressures of: (b) 1×10^{-3} Torr; (c) 1×10^{-2} Torr; (d) 1×10^{-1} Torr; (e) 2 Torr; (f) 100 Torr.

band is the same as in the absence of hydrogen. No influence of coadsorbed hydrogen on the linear CO band had been established previously for the Pt/Al_2O_3–CO–H_2 system (*19*). Evacuation of the cell almost restored the initial ir spectrum (Fig. 3a).

The decrease in band intensity (Fig. 2e) implies the existence of certain surface species formed during the interaction between CO and H_2. The reappearance of the initial CO bands after hydrogen evacuation (Fig. 2f) can then be explained by suggesting a subsequent decomposition of the corresponding surface species. In other experiments, aimed at high surface concentration of the expected species, a higher CO coverage (θ_{CO} = 0.8) and longer contact time were applied. Spectra observed at varying contact time are shown in Fig. 4. Comparatively intense bands appeared in the CH stretching region at 2850 and 2960 cm^{-1} (Figs. 4b, d). Upon evacuation these bands disappeared but the bands characteristic of CO adsorbed on Pd/Al_2O_3 appeared again (Fig. 4e) and this spectrum differed slightly from the initial one (Fig. 4a). Negligible reduction of transmission in the region 1300–1700 cm^{-1} was also found but no bands of measurable intensity were observed.

Another set of experiments was conducted with the aim of examining the influence of temperature on the ir spectrum of CO adsorbed on Pd/Al_2O_3 without and in the presence of hydrogen. In these experiments 2 Torr of CO was introduced into the ir cell and the sample was annealed at a certain temperature (Figs. 5a–e) or the sample was heated in a mixture of carbon monoxide and hydrogen at the same temperature (Figs. 5a′–e′). No significant changes of the spectra were observed up to about 150°C (Fig. 5e′). This behaviour can be predicted keeping in mind the ability of carbon monoxide to displace hydrogen from the palladium surface as previously

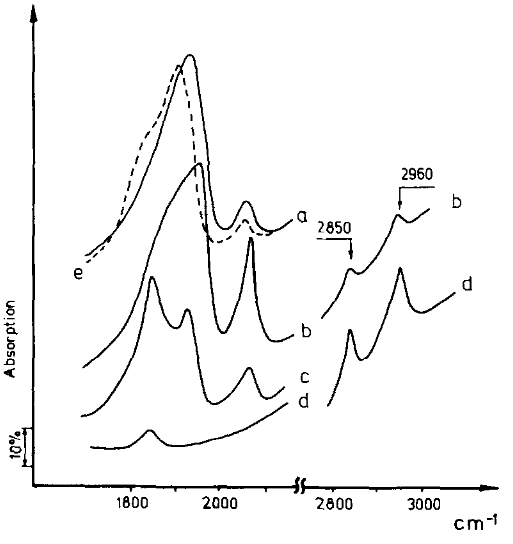


FIG. 4. Infrared spectrum of CO preadsorbed on Pd/Al_2O_3 and effect of contact time during hydrogen coadsorption: (a) CO adsorption at 35°C; θ_{CO} = 0.8; (b) hydrogen added at 35°C (P_{H_2} = 700 Torr); (c) 18 h after (b); (d) 90 h after (c); (e) after evacuation at 35°C down to 1×10^{-5} Torr.

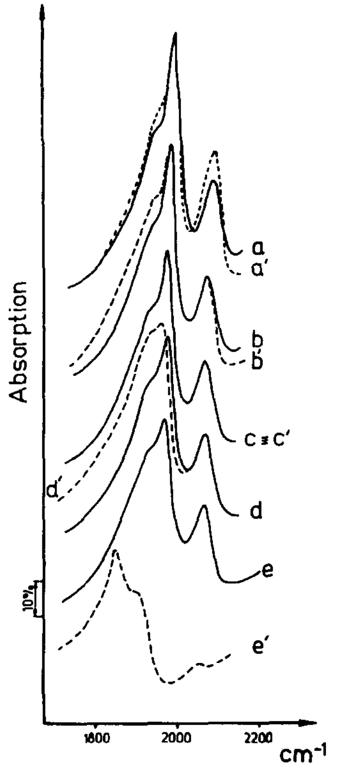


FIG. 5. Infrared spectra of Pd/Al_2O_3 during annealing in the presence of gaseous CO or in a mixture of CO and H_2: (a) to (e), CO added (P_{CO} = 2 Torr) and the sample heated at: (a) 35°C; (b) 85°C; (c) 115°C; (d) 130°C; (e) 150°C; (a') to (e'), a mixture of CO and H_2 added and the sample heated at the same temperatures as indicated above (CO:H_2 = 1:360; total pressure of 700 Torr). The spectra were recorded at the respective temperatures. The band denoted as e' completely disappeared a short time after the spectrum was taken.

established by LEED measurements (*21*). As the temperature reached 150°C gaseous CO was completely converted into methane (a band at 3019 cm^{-1} appeared) and the intensity of both the linear and bridge-bonded CO bands (2070 and 1980 cm^{-1}, respectively) was strongly reduced showing that the triply bonded species (a band at 1850 cm^{-1}) is the most unreactive one (Fig. 5e'). Since no more useful information about the nature of the CO–H_2 interaction could be obtained, the spectra in the CO stretching region are not presented in Figs. 6 and 7.

(*b*) *Interaction of Carbon Monoxide and Hydrogen on Pd/Al_2O_3 under Dynamic Conditions*

In this series of experiments the mixture of hydrogen and carbon monoxide was passed through the cell and the ir spectra were taken at various temperatures (Figs. 6, 7). Bands of moderate intensity appeared at 1480, 2850, and 2960 cm^{-1} in the case of a low CO/H_2 (1:350) ratio (Fig. 6). When this ratio was increased to 1:3 the spectra shown in Fig. 7 were observed. Bands at 1375, 1395, 1595, and 2920 cm^{-1} appeared and their intensity depended on temperature. Bands of lower intensities were also observed at 2850, 2960, and 3010 cm^{-1} (Figs. 7a, b). In both cases methane was found in the gas phase at elevated temperatures giving rise to an infrared band at 3019 cm^{-1} (Figs. 6d, e, and 7c).

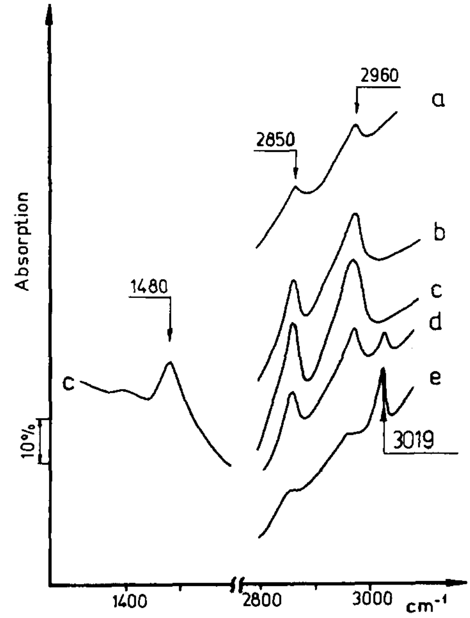


FIG. 6. Infrared spectra of a Pd/Al_2O_3 sample during CO and H_2 interaction under dynamic conditions: (a) a mixture of CO and H_2 passed through the ir cell at 35°C (CO:H_2 = 1:350; total pressure of 700 Torr); (b) to (e), heated at: (b) 95°C; (c) 115°C; (d) 135°C; (e) 155°C. The spectra were taken at the same temperatures. The band at 3019 cm^{-1} indicates the presence of methane in the gas phase.

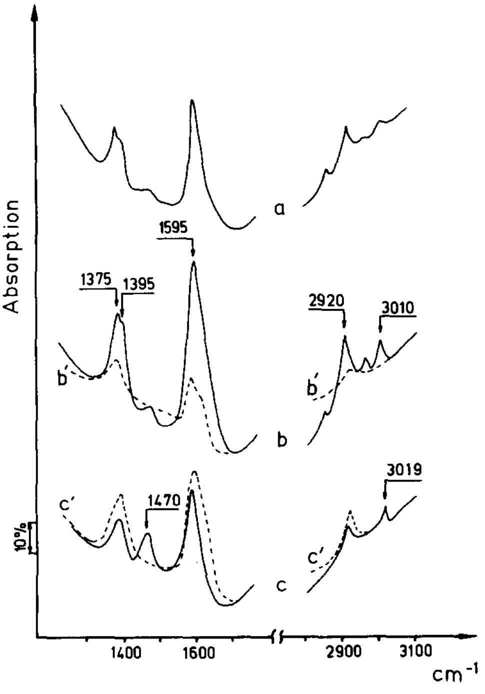
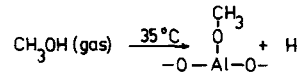


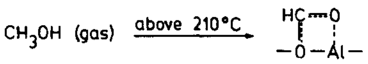
FIG. 7. Infrared spectra of Pd/Al_2O_3 during CO and H_2 interaction under dynamic conditions: (a) to (c), a mixture of CO and H_2 passed through the infrared cell at (a) 122°C; (b) 150°C; (c) 225°C ($CO:H_2$ = 1:3; total pressure of 700 Torr). The spectra were taken at the same temperatures. Broken lines (b', c') denote spectra recorded after a CO–H_2 mixture was passed over a pure alumina (Degussa) disk under the experimental conditions applied to Pd/Al_2O_3.

The bands recorded in both the CH stretching region and the region 1300–1700 cm^{-1} (Figs. 4, 6) were previously observed by Greenler in a study of methanol adsorption on alumina (*20*). In Fig. 8 the infrared spectra of methanol adsorbed on a pure alumina pellet after evacuation at various temperatures are shown. Upon heating and evacuation the intensities of the 2850- and 2960-cm^{-1} bands decreased while the intensities of the 1390- and 1590-cm^{-1} bands increased (Fig. 8). The frequencies of the bands from methanol adsorbed on pure alumina (Fig. 8) are identical to those observed during the interaction of carbon monoxide and hydrogen on Pd/Al_2O_3 (Figs. 4, 6). It should be emphasized, however, that even at 320°C the intensity of the bands from methanol adsorbed on alumina was still high (Fig. 8), whereas the respective bands observed with the Pd/Al_2O_3 sample strongly decreased and disappeared at quite lower temperatures (Figs. 6, 7).

Greenler suggested the following models for methanol adsorption on alumina (*20*):

 (1)

$$CH_3OH\,(gas) \xrightarrow{35\,°C} \underset{-O-Al-O-}{\overset{CH_3}{\overset{|}{O}}} + H \quad (1)$$

 (2)

$$CH_3OH\,(gas) \xrightarrow{\text{above } 210\,°C} \underset{-O-Al-}{\overset{HC\cdots O}{}} \quad (2)$$

Our experiments demonstrated that the surface species shown in (2) (bands at 1390 and 1590 cm^{-1}, Fig. 8c) occurred not only in the presence of methanol vapor at elevated temperatures (*20*) but also after decomposition of the methoxy species shown in (1) (bands at 1480, 2850, and 2960 cm^{-1}, Fig. 8a). Greenler (*20*) denoted the structure of this species as a formate-like one.

(*c*) *Interaction of CO and Hydrogen on a* Pd/SiO_2 *Catalyst*

In the previous paragraph it was shown that the interaction of carbon monoxide and hydrogen on Pd/Al_2O_3 produces certain bands in both the CH stretching region and the region 1300–1700 cm^{-1} (Figs. 4, 6, 7). The same bands are observed in the ir spectrum of methanol strongly adsorbed on alumina (Fig. 8). Hence, the question arises if these bands are due to surface species adsorbed on the support or on the metal component of the catalyst.

To resolve this problem the experiments already described with Pd/Al_2O_3 were repeated on a silica-supported Pd catalyst. No bands were observed in the regions mentioned above.

DISCUSSION

Recently Duš (*22, 23*) has studied hydrogen adsorption on Pd films by surface potential change measurements. In general, his results suggest that hydrogen exists in several forms which depend on the experimental conditions: adsorption temperature

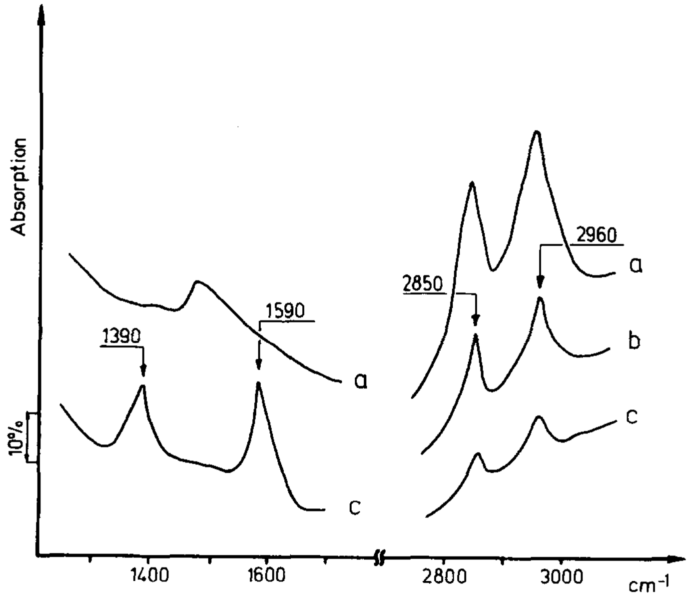


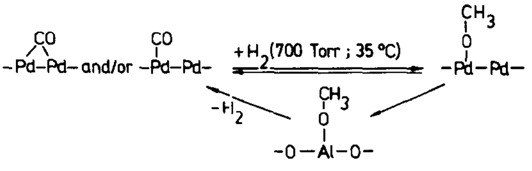
FIG. 8. Infrared spectra of methanol adsorbed on a pure alumina disk: (a) methanol added at 35°C (P_{CH_3OH} = 10 Torr) and evacuated down to 1×10^{-5} Torr at the same temperature; (b) annealing up to 200°C and evacuation after (a); (c) annealing up to 320°C and evacuation after (b).

and hydrogen pressure. Adsorption of hydrogen at 298 K and pressure of less than 1 Torr (the spectra shown in Figs. 3b–d were recorded under similar conditions) causes the formation only of an electronegative β^- form (*23*). Provided β^- hydrogen is coadsorbed with carbon monoxide on the Pd surface, an electron transfer from the metal–carbon bond to the metal would occur due to the competition for metal *d* electrons. Note that upon adsorption metal *d* electrons enter CO π^*-antibonding molecular orbitals thus decreasing the C–O bond order and ν_{CO} (*24*). Therefore, if metal *d* electrons are accepted by hydrogen, the force constant of the C–O bond is increased which results in increased ν_{CO} (Figs. 2b–d and 3b–f) in comparison with the case when hydrogen is absent (Figs. 2a and 3a). Thus the direction of the shift of the ir bands from CO preadsorbed on Pd/Al_2O_3 produced by hydrogen coadsorption is in agreement with the data obtained by surface potential measurements.

Two models can be proposed to describe the observed variation of relative intensity of the bands below 2000 cm^{-1} (Figs. 2, 3). These bands are later denoted as B_1 and B_2 and, as stated in the Introduction, they belong to the multiply bonded CO species on Pd(111) and Pd(100), respectively (Fig. 1a). According to the first model hydrogen affects the mobility of the adsorbed layer causing migration of CO molecules from Pd(100) to Pd(111): the intensity of the B_1 band is enhanced while the B_2 peak becomes smaller (cf. Figs. 2d, e; 3b–f). Considering the second model a rearrangement of the surface metal atoms may be suggested and we believe it is more suitable to explain the observed changes of the ir spectra (Figs. 2, 3). Using X-ray measurements Janko *et al.* (*25*) have found that repeated hydrogen treatment of randomly oriented polycrystalline Pd thin films leads to a low-temperature rearrangement of the Pd crystallites and to the formation of a (111) texture. The experiments have been carried out within the range of conditions characteristic of the formation and decomposition of the β-palladium hydride phase. In our experiments the appearance of preferable orientation results in a transformation of the mode of adsorbed CO (Figs. 2d, e and 3e, f): the intensity of the B_1 band (CO on Pd(111)) is increased at the expense of a reduction of the intensity of the B_2 band (CO on Pd(100)). These results are experimental evidence for structural modification of catalyst surfaces upon the action of adsorbates and are in agreement with previously reported ir band assignments for CO adsorbed on supported palladium (*9*).

Furthermore, the ir measurements conducted in the present study afford an opportunity to suggest a definite structure of the surface species formed during the interaction of CO and H_2. The spectra shown in Fig. 4 indicate that this interaction occurs even at room temperature since the bands from adsorbed CO disappear as contact time is increased (Figs. 4a–d). The bands arising in the CH stretching region (Figs. 4b, d) can then be assigned to vibration modes of surface species formed during the interaction of CO and H_2 on the palladium surface. However, identical bands are observed after methanol adsorption on pure alumina (Fig. 8) and they have been assigned by Greenler (*20*) to the vibrations of surface methoxyl groups (1). Therefore, it can be concluded that the interaction of CO and H_2 *on* palladium produces a surface species which is subsequently adsorbed on the alumina surface. By analogy with hydrogen spillover, this phenomenon can be compared with the migration of hydrogen species, atoms or ions, away from the metal onto the nonmetallic part of supported catalysts (*26*). Hence, in our experiments, alumina appears to be a "trap" for the surface species formed on the palladium surface.

The ir bands at 1480, 2850, and 2960 cm^{-1} were removed when the gas phase was evacuated. After outgassing, the spectrum in the CO stretching region (Fig. 4e) differed slightly from the initial one (Fig. 4a), indicating that the methoxy species on the alumina readsorbed and decomposed on the palladium surface thus yielding adsorbed CO again:



(3)

Demuth and Ibach (*27*) recently measured the electron energy loss spectrum of methoxy species on Ni(111) after methanol adsorption at 150 K and found that this species decomposes near room temperature. Most probably, the same is true for Pd/Al_2O_3. The methoxy species is unstable on the metallic surface at room temperature; it can occur on alumina in the presence of gas-phase hydrogen and is easily decomposed on the adjacent palladium atoms upon evacuation (3).

The experiments conducted under dynamic conditions demonstrated an interesting dependence of the CO/H_2 ratio on the type of surface species formed. Only bands characteristic of surface methoxyl groups adsorbed on alumina were observed with $CO : H_2 = 1 : 350$ (Figs. 6a–c) and they disappeared at elevated temperatures when methanation proceeded extensively (Figs. 6d, e).

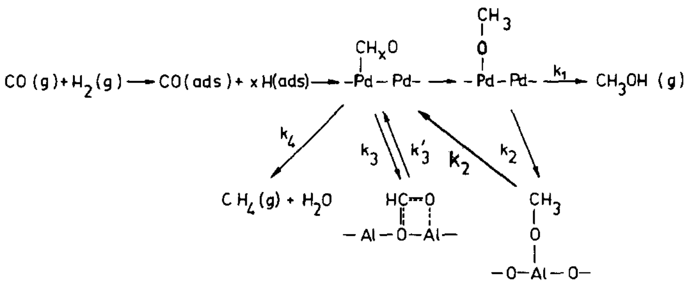
The spectra observed in the region 1300–1700 cm^{-1} with the higher CO/H_2 (1 : 3) ratio (Fig. 7) are in good agreement with those of aluminum formate (*28*) and formic acid adsorbed on alumina (*29*), indicating the occurrence of species of formate-like structure.

Parallel experiments were performed on

a pure alumina sample applying the same CO/H_2 ratios and temperatures. No ir bands were observed with the low CO/H_2 (1 : 350) ratio up to 210°C. With the high CO/H_2 (1 : 3) ratio still no bands were observed at 122°C, whereas, as already seen, the reaction mixture over Pd/Al_2O_3 gives rise to comparatively intense ir bands at the same temperature (Fig. 7a). At 150°C on pure alumina we observed bands identical to those produced on Pd/Al_2O_3, but their intensity was much lower (cf. Figs. 7b′ and b). Therefore, as in the case of the low CO/H_2 (1 : 350) ratio, it is relevant to suggest the existence of a spillover effect, i.e., hydrogen interacts with CO *on* Pd but the strongly adsorbed formate species occurs on alumina. At increasing temperature the intensity of the bands due to formate species on alumina was increased (Figs. 7b′, c′), in contrast to the case with Pd/Al_2O_3 (Figs. 7b, c) indicating that reverse spillover from Al_2O_3 to Pd predominates, resulting in methane formation (a band at 3019 cm^{-1}, Figs. 7b, c).

The bands characteristic of methoxy species at 2850 and 2960 cm^{-1} were also observed with the $CO : H_2 = 1 : 3$ ratio (Figs. 7a, b). Since they were less intense, the methoxy species appeared only to be a byproduct in this case. The band which appeared at about 2920 cm^{-1} (Figs. 7a, b) is probably due to the CH stretching vibration of the formate species. Kishi *et al.* (*30*) observed a band at about 2900 cm^{-1} after adsorption of formic acid on a Ni film and assigned it to ν(C–H) of the chemisorbed formate ion.

From the results discussed above it is clear that depending on the experimental conditions, the reaction of carbon monoxide and hydrogen proceeds via different pathways. A considerable excess of hydrogen leads to the fast formation of hydrogen-enriched oxygenated intermediates. Poutsma *et al.* (*31*) recently found that supported palladium catalysts gave methanol with high selectivity within a certain temperature–pressure regime. Since methanol synthesis is not thermodynamically favorable at the temperatures and pressures applied in the present work, the reaction produces methoxy species on palladium which is successively adsorbed on alumina (3). To summarize, the results of Poutsma *et al.* (*31*) and of this study can be presented in the following scheme:



(4)

Step k_1 occurs at temperatures of 275–350°C and pressures up to 1000 atm (*31*); k_2 and k_3 proceed at temperatures up to about 135°C and atmospheric pressure with $CO : H_2$ of 1 : 350 and 1 : 3, respectively. Methanation is significant above 135°C at atmospheric pressure via step k_4; also, both the formate and methoxy species adsorbed on Al_2O_3 decompose under these conditions on palladium through steps k_2' and k_3'.

As stated above, both the formate and methoxy species could also be formed on pure alumina after interaction between CO and H_2 (Figs. 7b′, c′) and are much more stable on the alumina than on the Pd/Al_2O_3 catalyst. For example, the formate species (bands at 1390 and 1590 cm^{-1}, Fig. 8c) occurs on the alumina after decomposition of the methoxy species (bands at 1480, 2850, and 2960 cm^{-1}, Figs. 8a–c), whereas it decomposes on Pd/Al_2O_3 to yield methane (a band at 3019 cm^{-1}, Figs. 6d, e) at much lower temperature (135°C).

Methanol is probably a reaction product of carbon monoxide hydrogenation when palladium hydride is formed as a consequence of hydrogen diffusion into the bulk of the metal under certain conditions (*31*). In our study the formation of palladium hydride is allowed under the conditions denoted in Figs. 4 and 6 when the methoxy species is formed. Perhaps, with $CO : H_2 = 1 : 3$ hydrogen diffusion is strongly inhibited and the species more deficient in H_2, namely, the formate species, is predominantly formed (bands at 1375, 1395, 1595, and 2920 cm^{-1}, Fig. 7).

It is relevant to suggest that the most stable species formed on palladium will be "trapped" on alumina. The most stable intermediates of methanol synthesis and methanation are different (4), being CH_3O for methanol formation and CHO for methanation. Hence an inference can be made that methane is formed through an independent pathway parallel to that of methanol synthesis. Moreover, taking into consideration the stability of the surface species formed, one can arrive at the conclusion that k_1 is the rate-limiting step of methanol formation, while k_4 ($x = 1$, (4)) is probably a step which controls the rate of methanation.

Further experiments are necessary to explain the reason for the difference in catalytic activity between alumina- and silica-supported palladium in the methanation reaction as found by Vannice and Garten (*14*). Preliminary results obtained in this laboratory demonstrated that no surface species was detected on the silica surface of Pd/SiO_2 (see Results). As already shown, the $CO–H_2$ interaction produces CHO intermediates on both the metallic surface of Pd/Al_2O_3 and pure alumina (bands at 1375, 1395, 1595, and 2920 cm^{-1}, Fig. 7); however, the reaction temperature is different.

Finally, the origin of the band at 1470 cm^{-1}, whose intensity is increased with increasing temperature (Fig. 7), will be briefly discussed. Recently Fujimoto *et al.* (*32*), using a reactive temperature-programmed desorption technique, have found formation of CO_2 on Ru/Al_2O_3 in the temperature range 370 to 670 K. The presence of CO_2 is attributed to CO disproportionation or to a reaction between adsorbed CO and H_2O formed by hydrogenation of other adsorbed carbon monoxide. Since disproportionation is not significant on palladium at temperatures up to 200°C, CO_2 is probably formed by the reaction between H_2O and CO and is subsequently adsorbed on the alumina. Thus the 1470-cm^{-1} band can be assigned to the vibration of unidentate carbonate formed on alumina as a result of CO_2 adsorption (*33*).

At present it is difficult to assign the band at 3010 cm^{-1} (Fig. 7a) and its origin will not be discussed in this paper.

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