JOURNAL OF CATALYSIS 83, 437–445 (1983)

Methanol Adsorption and Decomposition on Clean and Oxygen Precovered Palladium (111)

J. A. GATES AND L. L. KESMODEL[1]

Department of Physics, Indiana University, Bloomington, Indiana 47405

Received February 18, 1983; revised May 6, 1983

The interaction of methanol with Pd(111) has been studied using high-resolution electron energy loss spectroscopy (HREELS). We find both a chemisorbed and a physisorbed phase on the surface at 140 K. Desorption of the physisorbed phase occurs by 160 K and approximately 90% of the chemisorbed layer desorbs by 300 K. Exposure to methanol at 300 K causes dissociation to chemisorbed CO. Decomposition of chemisorbed methanol to a methoxy species occurs near 200 K in the presence of a preadsorbed p(2 × 2) oxygen layer whereas no methoxy is detected on the clean surface. Further dehydrogenation to CO is observed by 300 K on the oxygen precovered surface.

I. INTRODUCTION

The interaction of alcohols with single crystal metal surfaces has received much attention in the last 10 years (*1*, *2*). Alcohol-like intermediates are believed to be involved in Fischer–Tropsch synthesis reactions (*3*). Decomposition of alcohols on metal surfaces form such products as formaldehyde, carbon dioxide, and methyl formate (*1*).

Studies on Cu(110) (*4*) and Ag(110) (*5*) first identified a methoxide (CH_3O-) intermediate in methanol decomposition under the conditions of a single crystal substrate and an ultrahigh vacuum. Since then, methoxy has been identified using high-resolution electron energy loss spectroscopy (HREELS), ultraviolet photoemission spectroscopy (UPS), and other methods on Ni(111) (*6*), Cu(100) (*7*), Pt(111) (*8*), and Ni(100) (*9*). The relatively high stability of this intermediate on copper and silver has been related to the high selectivity for formaldehyde formation on these surfaces (*7*). Sexton (*8*) has suggested that methoxy stability is higher on surfaces with low heats of adsorption of CO and H_2. One important component in most of the above mentioned studies (*4*, *5*, *7*, *8*) is that preadsorbed oxygen enhances the stability of the methoxy intermediate presumably by offering a mechanism, H_2O formation, for the removal of the hydroxyl hydrogen atoms (*1*).

Studies on palladium surfaces are motivated by reports that this metal can catalyze methanol formation from carbon monoxide and hydrogen with high efficiency under certain conditions (*10*, *11*). Fajula *et al.* (*11*) found that while the competing methanation reaction is dependent on the catalytic support, methanol formation is dependent on the adsorption properties of the metal crystallites. Methanol adsorption has been studied with UPS on polycrystalline Pd foils (*12*) and with UPS, thermal desorption spectroscopy (TDS), low energy electron diffraction (LEED), HREELS, and work function measurements on clean Pd(100) (*13*). While the latter work contains more detail, results indicate that at low temperatures methanol adsorbs "intact" and then mainly desorbs by 300 K.

We have studied the interaction of methanol with clean and oxygen covered Pd(111) surfaces using HREELS over a wide temperature range. In agreement with the previous investigation on Pd(100) (*13*),

---

[1] To whom correspondence should be addressed.

0021-9517/83 $3.00

we find that methanol chemisorbs at low temperatures (~140 K) and then mostly desorbs from the surface by 300 K. Methanol exposure at 300 K results in dissociative adsorption in the form of CO and H as reported on Pd foils (*12*). The presence of preadsorbed oxygen, however, allows the formation of a methoxy species near 200 K. This species then decomposes to adsorbed CO by 300 K.

II. EXPERIMENTAL METHODS

Experiments were performed in a stainless-steel, ion-pumped ultrahigh vacuum system (base pressure 10^{-10} Torr (1 Torr = 133.3 N m^{-2})). The chamber is equipped with Varian LEED/Auger electron optics, a UTI quadrupole mass spectrometer, and an ion bombardment gun in addition to the high-resolution electron spectrometer. The spectrometer is a cylindrical 127° monochromator and analyzer system described elsewhere (*14*). A beam energy of 3.3 eV was used to maximize the signal. Resolution varied between 70 and 90 cm^{-1} throughout the experiment. Initially, spectra were obtained after the sample cooled to less than 150 K. However, this was found to give misleading results due to the combination of background methanol gas in the vacuum chamber and the long cool-down time (~30 min). As noted below, fast (~10 min) scans of the spectrum immediately after heating gave more accurate results. All spectra were observed repeatedly and frequency values given here were reproducible within 10 cm^{-1}. (The exception is the broad OH stretching band on the oxidized surface which has an uncertainty of 18 cm^{-1}.)

The palladium sample was cut to within $\frac{1}{2}$° of the (111) surface from a single crystal cylinder ~1 cm^2 in diameter and polished down to 0.25 μm grit size using standard crystallographic techniques. A tungsten filament mounted behind the sample was used for heating. Cooling was accomplished with liquid nitrogen. A chromel-alumel thermocouple was mounted on the sample holder next to the crystal. During the experiment, thermocouple readings were held constant for 5 min to assure that the crystal surface reached the desired temperature. Initial cleaning of the Pd(111) sample was described elsewhere (*14*). Routine cleaning consisted of 500 eV argon ion bombardment and annealing to ~600°C.

Vapor pressure reagent grade CH_3OH and CD_3OD were used. The purity was checked with the mass spectrometer through comparison with the known cracking pattern of methanol (*15*). Sample dosing occurred through a leak valve into the main vacuum chamber. Pressure readings during methanol exposure were divided by 1.9 to correct for ion gauge sensitivity (*16*).

III. RESULTS

A. Interaction of CH_3OH and CD_3OD with Clean Pd(111)

Vibrational spectra obtained from exposure of Pd(111) to methanol and deuterated methanol are shown in Fig. 1. Saturation coverage could be attained at 140 K and resulted in the lower curves (c,f). We typically used a 30 L (1 L = 10^{-6} Torr-sec) exposure although HREELS spectra did not change after ~5 L. Frequency values and assignments are tabulated along with those of liquid phase methanol (*17*) in Table 1. The close agreement indicates that a condensed layer exists on the palladium surface at this temperature. The vibrational spectrum of vitreous solid methanol (*18*) is very similar to that of the liquid phase. Both spectra are characterized by broad OH stretching and out-of-plane bending bands resulting from hydrogen bonding. These features are also evident in Figs. 1c and f. The OH stretching frequency on palladium is close to the liquid phase value and 100 cm^{-1} higher than in the solid phase. Observation of the LEED pattern showed that since increased exposure intensifies the background but produces no new features, methanol does not form a long range ordered structure on Pd(111).

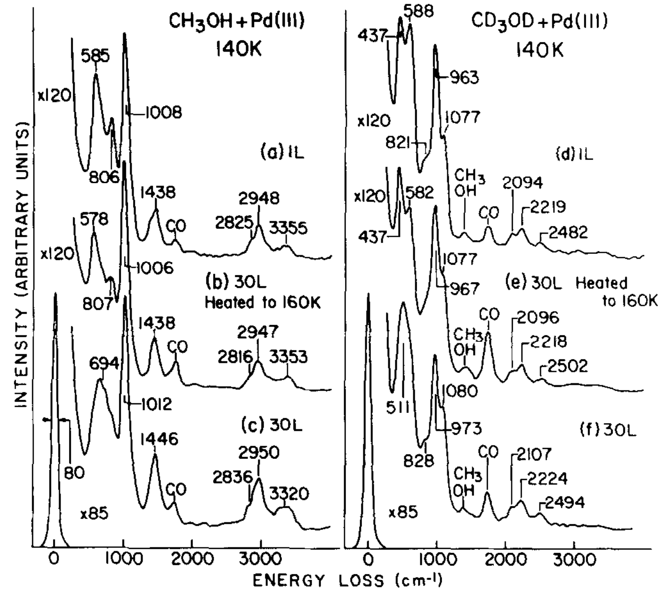

FIG. 1. Vibrational spectra of methanol and deuterated methanol on Pd(111) at 140 K. Curves c and f correspond to the condensed phase. The chemisorbed phase is obtained both by heating the condensed layer (b,e) and by using a lower exposure (a,d).

Heating the condensed layer to 160 K leaves a chemisorbed monolayer (Figs. 1b,e). Similar spectra resulted from a 1 L exposure at 140 K as seen in Figs. 1a and d. The appearance of OH and CH_3 stretching modes, a CH_3 deformation mode, and a CO stretching mode indicate that methanol is associatively chemisorbed on Pd(111). Frequency values and assignments are given in Table 2 along with corresponding data on

TABLE 1

Vibrational Frequencies (±10 cm^{-1}) of Condensed Methanol on Pd(111) at 140 K[a]

Assignment	Liquid	Condensed CH_3OH	Condensed CD_3OD	Ratio
OH stretch	3328	3320	2495	1.33
CH_3 deg. stretch	2980	2950	2225	1.33
	2946			
CH_3 sym. stretch	2834	2835	2105	1.35
CH_3 deg. deform.	1480	1445	1080	1.34
CH_3 sym. deform.	1450			
OH in plane bend	1418			
CO stretch	1030	1010	975	1.04
CH_3 asym. rock	1165	~1120[b]	830	1.35
CH_3 sym. rock	1115			
OH out of plane bend[c] CO torsion[c]	655	695	510	1.36

[a] Liquid phase values are from Ref. (17).

[b] Weak shoulder.

[c] Mixed mode (31).

TABLE 2

Vibrational Frequencies (±10 cm^{-1}) and Approximate Mode assignments of Chemisorbed Methanol on Pd(111) with and without Preadsorbed Oxygen[a]

Assignment	CH_3OH (CD_3OD)	Ratio	O_2/CH_3OH (O_2/CD_3OD)	Ratio
OH stretch	3355 (2480)	1.35	3250(b) (2430(b))	1.34
CH_3 deg. stretch	2950 (2220)	1.33	2940 (2200)	1.34
CH_3 sym. stretch	2825[b] (2095)	1.35	2825[b] (2085)	1.35
CH_3 deg. deform. CH_3 sym. deform. OH in plane bend	1440 (1075)	1.34	1445 (1090)	1.32
CO stretch	1010 (965)	1.05	1025 (975)	1.05
CH_3 asym. rock	~1110[c] (820)	—	— (~800[c])	
CH_3 sym. rock	805 (590)	1.37	855 (615)	1.38
OH out of plane bend[d] CO torsion[d]	585 (435)	1.34	520[e] (465)	—

[a] Values correspond to 1 L exposure to methanol. Oxygen exposure is 8 L.

[b] Shoulder.

[c] Weak shoulder.

[d] Mixed mode. The other such mode is predicted to be at 173 cm^{-1} in crystalline methanol (*31*).

[e] Broad peak also containing adsorbed oxygen O–M stretching mode (474 cm^{-1}).

the oxygen covered surface referred to in the next section.

We also exposed the clean Pd(111) surface to methanol at 300 K with results shown in Fig. 2. In this case, methanol dissociates to CO upon adsorption as evidenced by characteristic modes at 1822 cm^{-1} (ν_{CO}) and 329 cm^{-1} (ν_{CM}). This species desorbs at 450–500 K in good agreement with TDS studies of CO on palladium (*19*). Decomposition to adsorbed CO at 300 K is also in agreement with UPS results on polycrystalline Pd (*12*). Surface hydrogen, although expected from TDS data on other surfaces (*13, 20, 21*), is not clearly detected in our spectra. Hydrogen adsorption on clean Pd(111) results in a weak mode near 450 cm^{-1} at low temperatures (~150 K). At higher temperatures hydrogen is believed to occupy subsurface sites (*22*) and the HREELS spectrum is too weak to observe. A weak feature seen near 500 cm^{-1} in Fig. 2b may be due to adsorbed hydrogen. However, this peak is not distinguishable from noise in many of our spectra and may also be caused by an oxygen impurity.

As seen in Fig. 2a, heating low temperature chemisorbed methanol past ~200 K causes most of the surface species to desorb. Preliminary data erroneously indicated dissociation of the surface species to CO at higher temperatures. However, by recording fast spectra (~10 min) without waiting for the sample to cool, we found that most, if not all, of the observed CO was derived from *background methanol* in the chamber. After heating, we continuously observed the vibrational spectra until the sample was below 150 K. The peak near 1800 cm^{-1} reached a maximum intensity and then chemisorbed methanol features appeared at lower temperatures.

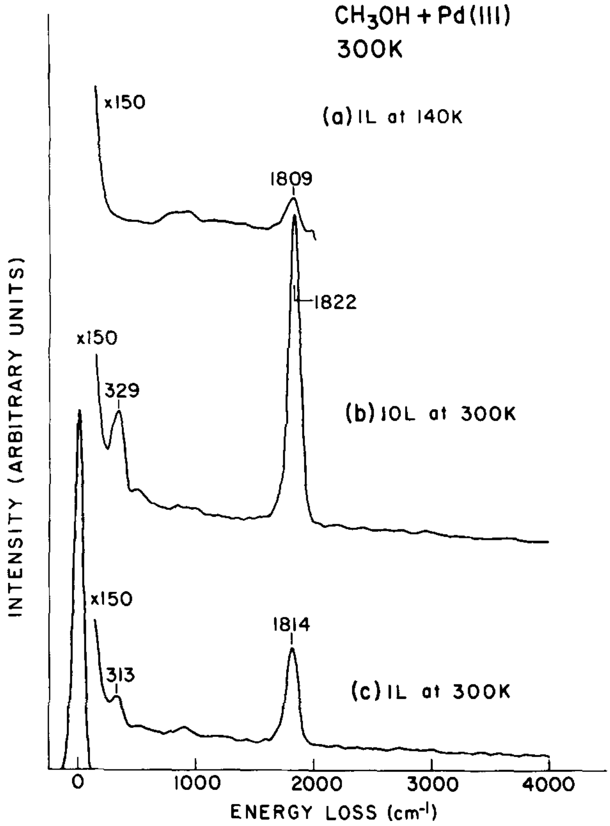

FIG. 2. Vibrational spectra of adsorbed CO obtained after exposure of Pd(111) to methanol at 300 K. The top curve is a result of heating chemisorbed methanol to 300 K.

B. Interaction of CH_3OH and CD_3OD with Pd(111)-p(2 × 2) O

The bottom curves (d and h) in Fig. 3 show the vibrational spectrum of an 8 L exposure to O_2 at 300 K. This corresponds to a p(2 × 2) LEED pattern ($\theta = 0.25$) in agreement with Conrad *et al.* (*23*). Oxygen dissociatively adsorbs at 300 K giving an oxygen–metal stretching frequency at 475 cm^{-1}. The oxygen atoms are believed to occupy the threefold hollow sites on the (111) surface (*23*).

Saturation coverage of methanol and deuterated methanol on the oxygen-covered surface at 140 K exhibits the vibrational spectra shown in Figs. 3c and g. Comparison with Fig. 1 shows that an oxygen layer inhibits condensation, but not chemisorption. We note that the strong loss at 520 cm^{-1} (Fig. 3c) appears to be a composite of the atomic oxygen–metal stretch at 475 cm^{-1} and the methanol bending mode near 578 cm^{-1} (Fig. 1b). There is a significant shift and broadening in the OH stretching region in the presence of oxygen. Frequencies and assignments for chemisorbed CH_3OH and CD_3OD are given in Table 2.

Dissociation to methoxy occurs by 200 K (Figs. 3b,f) as indicated by several characteristic spectral changes. The OH stretching mode has disappeared and a metal–oxygen mode has appeared at 302 cm^{-1}. The high intensity CO stretching mode (1041 cm^{-1}) suggests that this bond is close to perpendicular to the surface. Some atomic oxygen remains on the surface giving rise to the loss at 479 cm^{-1}. Frequency data for the methoxy species are enumerated in Table 3.

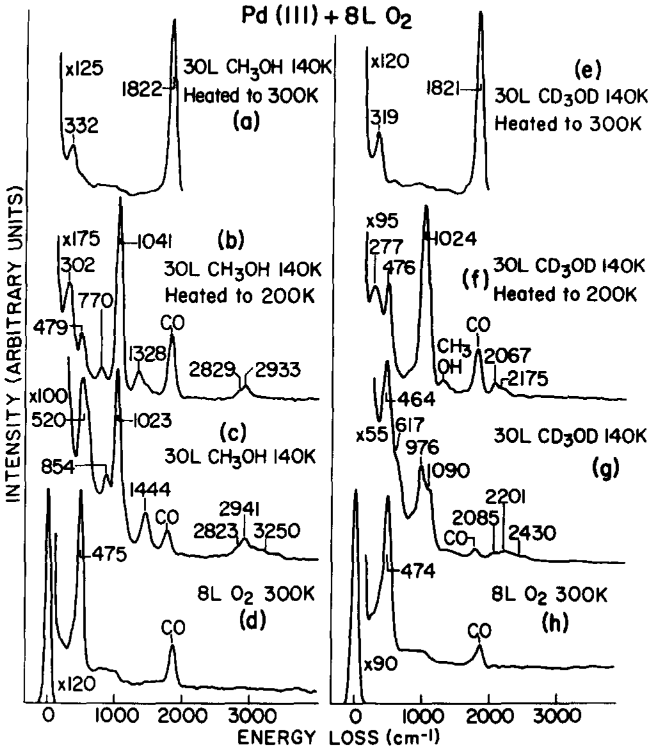

FIG. 3. Vibrational spectra of CH_3OH and CD_3OD adsorption on a p(2 × 2) oxygen covered Pd(111) surface. Curves b and f are identified with the methoxy (CH_3O-) species. Decomposition to CO occurs by 300 K (a,e).

By 300 K, the surface species is CO (Figs. 3a,e). These spectra were obtained, as explained in the last section, immediately after heating. It is clear that atomic surface oxygen provides a mechanism for the formation of CO from adsorbed methanol, via a methoxy intermediate.

TABLE 3

Vibrational Frequencies (±10 cm^{-1}) of Methoxy on Pd(111)

Assignment	CH_3O	CD_3O	Ratio
CH_3 deg. stretch	2935	2175	1.35
CH_3 sym. stretch	2830	2065	1.37
CH_3 deform.	1330	—	
CO stretch	1040	1025[a]	1.02
CH_3 rock	770	—	—
O-Pd stretch	300	275	1.09

[a] Broad peak probably also containing CH_3 deformation mode.

IV. DISCUSSION

Christmann and Demuth (*13*) conducted a detailed study of methanol adsorption at low temperatures on Pd(100). They were able to distinguish the first physisorbed layer from subsequent layers by slightly different desorption temperatures of ~145 K and ~142 K. We associate the condensed spectra of Figs. 1c and f with this first physisorbed layer for several reasons. First, we adsorbed near the desorption temperature of condensed methanol on both Pd(100) (142 K) (*13*) and Pt(111) (140 K) (*8*). Second, we observe saturation of the condensed phase. On Cu(100) (*7*), there is a continuous degradation of the HREELS elastic beam intensity with increased methanol exposure at 100 K. We observed no change after ~5 L. Substrate LEED features eventually disappear with increased condensation on Pd(100) at 77 K (*13*), but not on Pd(111) at 140 K. Finally, we did not obtain a physisorbed phase in the presence of preadsorbed oxygen, an effect which is not expected under conditions favorable to multilayer formation (*7*, *8*).

In Table 4, we have compared the vibrational frequencies of chemisorbed methanol on several substrates. UPS work has shown that methanol is weakly chemisorbed via the oxygen lone-pair orbital on Ni(111) (*20*), Pd(100) (*13*), polycrystalline Pd (*12*), and Cu(110) (*24*). The close agreement in vibrational frequencies indicates the same bonding scheme on Pd(111). While we did not carry out quantitative work function measurements, we did find it necessary to apply a negative potential to the crystal to compensate for the work function decrease due to the chemisorbed layer. This also supports a bonding model placing the negative (oxygen) end of the molecule closest to the surface.

We should point out that Christmann and Demuth (*13*) reported the formation of methoxy at low temperature for very low CH_3OH exposures (~0.05 L) on Pd(100). We found the effects of such low coverages very difficult to reproduce in our system. Peaks in the CH_3 and OH stretching regions of the spectrum were not visible above background. However, we did find a loss peak near 300 cm^{-1} which may be the oxygen–metal bond mode in methoxy, but we cannot confidently eliminate the role of surface defects in the formation of this species.

As on Pt(111) (*8*), Cu(100) (*7*), Cu(110) (*4*), and Ag(110) (*5*), we find that surface oxygen stabilizes methoxy on Pd(111). This species remains on Ag(110) (*5*), Cu(100) (*7*), and Cu(110) (*4*) at temperatures in excess of 400 K whereas decomposition to CO and H_2 occurs by 300 K on platinum (*8*) and palladium. It has been suggested that the stability of methoxy is related to a low heat of adsorption of CO and H_2 (*8*). The only exception to this has been the observation of methoxy at 300 K on Ti(001) (*25*).

Wachs and Madix have confirmed that surface oxygen removes the hydroxyl hydrogen from methanol to form water on Cu(110) (*4*) and Ag(110) (*5*). Likewise, water is observed to desorb from Pt(111) after methoxy formation (*8*). We find that methanol reactions with Pd(111) are similar to Pt(111) in that methoxy can only be identi-

TABLE 4

Vibrational Frequencies of Chemisorbed Methanol on Various Substrates[a]

Assignment	Liquid (*17*)	Pd(111)	O_2/Pd(111)	Pd(100) (*13*)	Pt(111) (*8*)	Ni(111)[b] (*32*)
OH stretch	3328	3355	3250	3345	3280	3330
CH_3 deg. stretch	2980	2950	2940	2945		2950
	2946				2930	
CH_3 sym. stretch	2834	2825[c]	2825[c]	2845		2825
CH_3 deg. deform.	1480	1440	1445	1470	1430	1460
CH_3 sym. deform.	1450			1400–1500		1390
OH in plane bend	1418			—		
CO stretch	1030	1010	1025	1025	1000	1030
OH out of plane bend[d] CO torsion[d]	655	585	520[e]	500–800	700	750

[a] Only characteristic modes are given.

[b] Similar spectrum also reported for methanol on Ni(111) in Ref. (*6*). Ibach and Mills (*32*) suggest that earlier spectra were affected by H_2O impurity.

[c] Shoulder.

[d] Mixed mode (*31*).

[e] Broad peak also containing adsorbed oxygen O–Pd stretching mode (~475 cm^{-1}).

fied on the oxygen covered surface after heating chemisorbed methanol to 170–200 K. Higher temperature behavior with and without adsorbed oxygen is also analogous on the two substrates. Therefore, it is likely that water formation accompanies methanol dehydrogenation on Pd(111). Our inability to observe chemisorbed H_2O in our vibrational spectra could be for two reasons. First, desorption of water may occur before 200 K since it desorbs from Pt(111) ~190 K (*8*). However, our spectra seem to change continuously from 140 to 200 K with no indication of a different species. Second, vibrational modes of water may be much weaker than methoxy modes on Pd(111). This is indeed the case with platinum (111) on which water adsorption has been studied using HREELS (*26*). A similar study on Pd(111) would be instructive on this point since it is conceivable that although we do not see an OH stretching vibration in Fig. 3b, the peak at 770 cm^{-1} is in close agreement with the stronger water libration mode on Pt(111) (*26*).

It is interesting to note that the only significant difference between the vibrational spectra of chemisorbed methanol on clean and oxygen covered Pd(111) surfaces (Figs. 1a and 3c) is in the OH stretching region. The shift and broadening of this mode in the presence of oxygen shows that there is hydrogen bonding between oxygen and hydroxyl hydrogen atoms prior to complete cleavage of the OH bond as suggested by Bowker and Madix (*24*). Similar behavior of CH stretching modes has been associated with higher temperature CH bond breaking in other systems (*8, 27*).

Although oxygen does not desorb from palladium below 300 K, the metal–oxygen vibrational mode at 475 cm^{-1} disappears when the methoxy-covered surface is heated to 300 K (Figs. 3a and e). This is most likely the result of the reaction between oxygen and carbon monoxide to form gaseous carbon dioxide. Desorption of CO_2 formed in this way is known to occur below 300 K (*28*). Furthermore, this reaction is believed to proceed via adsorbed states of both reactants (*29*).

Heating chemisorbed methanol on the clean surface resulted primarily in desorption on Pd(100) (*13*), Pt(111) (*8*), and Cu(100) (*7*). About 5% of the methoxy observed on the oxygen-covered surface is formed on clean Cu(100) after heating physisorbed methanol ice (*7*). Near 200 K, desorption claims an estimated 80% and >90% of the monolayer coverage on Pd(100) (*13*) and Pt(111) (*30*), respectively. From published spectra, it appears that similar results were found on Ni(111) (*6, 20*). Except for copper and silver, where methoxy is stable at high temperatures (*4, 5, 7*), the primary decomposition product of the remaining surface species is CO (*6, 8, 13*). We also find that most, if not all, of the chemisorbed monolayer on Pd(111) desorbs by 300 K. We do not detect any species other than CO on the surface at this temperature (Fig. 2). As mentioned earlier, a problem with CH_3OH and CO background pressure (even at chamber pressures below 10^{-9} T) prevented us from quantifying small changes in the intensity of the CO stretching mode. By assuming an efficient decomposition of methoxy to CO on the oxygen-covered surface, we estimate that no more than 10% of the original chemisorbed monolayer decomposes to CO by 300 K on the clean surface. A similar problem with background methanol pressure was reported by Hanson *et al.* (*25*).

In conclusion, we find that at 140 K methanol forms both chemisorbed and physisorbed layers on Pd(111). The weak chemisorption bond is through the oxygen lone-pair orbital. This bond is not specific to the substrate as seen in the agreement between vibrational frequencies on different substrates (Table 4). A methoxy intermediate can be formed at 200 K in the presence of surface oxygen probably via the mechanism first proposed by Wachs and Madix (*4*):

$$2(CH_3OH)_{ads} + (O)_{ads} \rightarrow 2(CH_3O)_{ads} + (H_2O)_{ads}$$

Complete dehydrogenation of methoxy to CO occurs by 300 K as observed on other group VIII elements (*6, 8*). On the clean Pd(111) surface, methanol desorbs at a lower temperature than required for decomposition. At higher temperatures, gaseous methanol does dehydrogenate to adsorbed CO on Pd(111) as on Pd(100) (*13*). Therefore, surface oxygen makes decomposition of the adsorbed species possible.

ACKNOWLEDGMENT

This work was supported by the Office of Naval Research.

REFERENCES

1. Madix, R. J., *Adv. Catal.* **29,** 1 (1980).
2. Sexton, B. A., *Appl. Phys.* **A26,** 1 (1981).
3. Rofer-DePoorter, C. K., *Chem. Rev.* **81,** 447 (1981).
4. Wachs, I. E., and Madix, R. J., *J. Catal.* **53,** 208 (1978).
5. Wachs, I. E., and Madix, R. J., *Surf. Sci.* **76,** 531 (1978).
6. Demuth, J. E., and Ibach, H., *Chem. Phys. Lett.* **60,** 395 (1979).
7. Sexton, B. A., *Surf. Sci.* **88,** 299 (1979).
8. Sexton, B. A., *Surf. Sci.* **102,** 271 (1981).
9. Baudais, F. L., Borschke, A. J., Fedyk, J. D., and Dignam, M. J., *Surf. Sci.* **100,** 210 (1980).
10. Poutsma, M. L., Elek, L. F., Ibarbia, P. A., Risch, A. P., and Rabo, J. A., *J. Catal.* **52,** 157 (1978).
11. Fajula, F., Anthony, R. G., and Lunsford, J. H., *J. Catal.* **73,** 237 (1982).
12. Luth, H., Rubloff, G. W., and Grobman, W. D., *Surf. Sci.* **63,** 325 (1977).
13. Christmann, K., and Demuth, J. E., *J. Chem. Phys.* **76,** 6308 (1982); **76,** 6318 (1982).
14. Kesmodel, L. L., Gates, J. A., and Chung, Y. W., *Phys. Rev.* **B23,** 489 (1981); Kesmodel, L. L., and Gates, J. A., *Surf. Sci.* **111,** L747 (1981).
15. "Atlas of Mass Spectral Data" (E. Stenhagen, S. Abrahamson, and F. W. McLafferty, Eds.), Vol. I. Interscience, New York, 1969.
16. Summers, R. L., NASA Technical Note TN D-5285 (1969).
17. Shimanouchi, T., "Tables of Molecular Vibrational Frequencies Part I." NSRDS-NBS6, Washington, D.C., 1967.
18. Falk, M., and Whalley, E., *J. Chem. Phys.* **34,** 1554 (1961).
19. Davies, P. W., and Lambert, R. M., *Surf. Sci.* **111,** L671 (1981).
20. Rubloff, G. W., and Demuth, J. E., *J. Vacuum Sci. Technol.* **14,** 419 (1977).
21. Johnson, S., and Madix, R. J., *Surf. Sci.* **103,** 361 (1981).
22. Eberhardt, W., Greuter, F., and Plummer, E. W., *Phys. Rev. Lett.* **46,** 1085 (1981).
23. Conrad, H., Ertl, G., Kuppers, J., and Latta, E. E., *Surf. Sci.* **65,** 245 (1977).
24. Bowker, M., and Madix, R. J., *Surf. Sci.* **95,** 190 (1980).
25. Hanson, D. M., Stockbauer, R., and Madey, T. E., *J. Chem. Phys.* **77,** 1569 (1982).
26. Sexton, B. A., *Surf. Sci.* **94,** 435 (1980).
27. Demuth, J. E., Ibach, H., and Lehwald, S., *Phys. Rev. Lett.* **40,** 1044 (1978).
28. Conrad, H., Ertl, G., and Kuppers, J., *Surf. Sci.* **76,** 323 (1978).
29. Engel, T., and Ertl, G., *J. Chem. Phys.* **69,** 1267 (1978).
30. Rendulic, K. D., and Sexton, B. A., *J. Catal.* **78,** 126 (1982); Sexton, B. A., Rendulic, K. D., and Hughes, A. E., *Surf. Sci.* **121,** 181 (1982).
31. Dempster, A. B., and Zerbi, G., *J. Chem. Phys.* **54,** 3600 (1971).
32. Ibach, H., and Mills, D. L., "Electron Energy Loss Spectroscopy and Surface Vibrations," p. 322. Academic Press, New York, 1982.