JOURNAL OF CATALYSIS 146, 22–33 (1994)

FTIR Study of the Interaction of Methanol with Clean and Potassium-Doped Pd/SiO_2 Catalysts

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Received May 14, 1993; revised July 26, 1993

The adsorption and dissociation of methanol on pure and K-promoted Pd/SiO_2 catalysts were investigated by means of FTIR spectroscopy. Spectra were registered at 213–523 K. Absorption bands due to molecularly adsorbed methanol were detected at 213–253 K, whereas methoxy formation was observed at and above 253 K. It appeared that most of the adsorbed methanol and methoxy species were located on the silica support, and only a very small fraction were bonded to the Pd. However, the presence of palladium induced the decomposition of adsorbed methanol even at 233 K, to give CO multiply coordinated to Pd, and CH_3CHO. The formation of adsorbed CH_3 species was also detected. Addition of potassium did not change the pathways of methanol dissociation, but led to stabilization of the methoxy and acetaldehyde. © 1994 Academic Press, Inc.

1. INTRODUCTION

Supported Pd is an effective and selective catalyst in CH_3OH synthesis, via the hydrogenation of both CO and CO_2 (1, 2). A great amount of work has been devoted to establishing the mechanisms of the reactions and to improving catalytic performance by variation of the supports and by adding different promoters to the catalysts (3). In the last decade, the interaction of CH_3OH with various Pd crystal faces has also been investigated under UHV conditions (4–14). It was considered that an evaluation of the nature of the methanol reaction intermediates on well-defined Pd surfaces would provide an important insight into the mechanism of CH_3OH synthesis.

Whereas numerous results have suggested that the primary step in the dissociation of CH_3OH is rupture of the O–H bond, recent findings have shown that both O–H and C–O bonds are cleaved in the dissociation of CH_3OH adsorbed on the Pd(111) surface (9, 14). As a result, we must consider the formation not only of CH_3O, but also of CH_3. However, since rupture of the C–O bond on the Pd(100) surface has not been observed, or at least only to a limited extent (11), it appears that the pathway of CH_3OH dissociation is a structure-sensitive reaction.

The present study examines the adsorption of CH_3OH on a supported Pd catalyst by means of FTIR spectroscopy. Attention is focused on the pathways of CH_3OH dissociation and on the adsorbed intermediates formed. Additionally, the effects of an alkali metal additive on the reaction modes of the surface complexes are also investigated.

2. EXPERIMENTAL

The catalysts were prepared by incipient wetting of silica (Cabosil) or alumina (Degussa) with an aqueous solution of palladium chloride (Ventron) or an aqueous mixture of palladium chloride and potassium nitrite (Reanal), respectively. The following catalysts were produced: 10 wt% Pd/SiO_2, 10 wt% Pd + 2.5 wt% K/SiO_2, 10 wt% Pd/Al_2O_3, and 10 wt% Pd + 5 wt% K/Al_2O_3. After impregnation, the samples were dried in air at 373 K. For IR studies, the dried powders were pressed into self-supporting wafers (30 × 10 mm, 10 mg/cm^2). The pretreatment of samples were performed in a vacuum IR cell: the samples were (a) heated (20 K/min) to 673 K under continuous evacuation, (b) oxidized with 100 Torr of O_2 (133 Pa) for 30 min at 673 K, (c) evacuated for 15 min, and (d) reduced in 100 Torr of H_2 for 60 min at 673 K. This was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment. During all these pretreatments, gases were circulated by a small magnet and the water formed was collected in a trap cooled by liquid nitrogen.

CH_3OH (Reanal, 99% purity) was purified by fractional distillation and stored in a glass bulb. To check the purity of the SiO_2 used in our experiments, an ICP (inductively coupled plasma) atomic emission spectroscopic study was performed. Zn (0.00128%), Ni (0.00076%), Fe (0.00053%), and Co (0.00002%) were detected. Tests for Mg, Al, Ca, Ba, Ti, Na, K, Li, Cu, and Cd were negative.

Infrared spectra were recorded with a Biorad (Digilab

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0021-9517/94 $6.00

Div.) Fourier transform IR spectrometer (FTS 7) with a wavenumber accuracy of ±2 cm^{-1}. Typically 16 scans were registered. All subtractions of the spectra in the present work were made without a scaling factor (f = 1.0000).

3. RESULTS

3.1. Adsorption of Methanol on Pd/SiO$_2$

Figure 1 shows the infrared spectrum of gaseous CH_3OH (1 Torr). The spectrum is consistent with the literature data (15). Absorption bands and their assignments are listed in Table 1.

Low-temperature adsorption. The spectrum obtained in the presence of 10% Pd/SiO$_2$ at 213 K displayed new bands (not observed in the spectrum of gaseous CH_3OH) at 3005–2988, 2922 and 1715 cm^{-1}, which may be due to adsorbed species formed in the surface reactions of CH_3OH (Fig. 2). Small shifts were registered in the positions of the bands of gaseous CH_3OH (in the C–H stretching and C–H deformation regions).

Heating the sample in CH_3OH resulted in the diminution of most of these bands, but they were seen in the spectra up to 293 K (Fig. 2); they were eliminated only when the sample was heated to 473 K. The band at 1715 cm^{-1} behaved differently; its intensity first increased up to 233 K and then remained practically constant up to room temperature. At and above 233 K, new bands appeared at 2155, 2071, 1973, and 1916–1900 cm^{-1}, indicating the occurrence of a surface reaction.

In the OH region, the spectral changes suggested the formation of hydrogen bonding at low temperatures (213–253 K); this was exhibited in the development of a broad band centered at around 3435 cm^{-1}. The negative absorption at 3744 cm^{-1} in the difference spectra (this band is characteristic of the OH groups on the silica surface) points to the fact that surface OH groups on the silica are involved in this process. At 273–293 K, the broad band disappears. The remaining small negative absorption band at 3744 cm^{-1} proves that the OH groups on the silica are consumed in the formation of H-bonding and in the subsequent desorption processes.

When the sample was evacuated at 213 K following the adsorption of CH_3OH, the observed absorption bands decreased somewhat in intensity, but their positions remained practically the same (Fig. 3). When the adsorbed layer was heated under constant evacuation, the bands due to adsorbed methanol attenuated more quickly than in CH_3OH vapor. The bands at 2998, 2956, 2931, 2920, and 2846 cm^{-1} could be distinguished clearly at low temperatures (213–243 K). It should be mentioned that, except for the 1450 cm^{-1} band, all bands in the 1500–1300 cm^{-1} region disappeared at 253 K, and at the same temperature the 2848 cm^{-1} band shifted to 2857 cm^{-1}. In the C–H stretching region, the bands at 2998 and 2931 cm^{-1} were also eliminated. The bands remaining in the spectra could be detected even at the highest temperature (293 K)

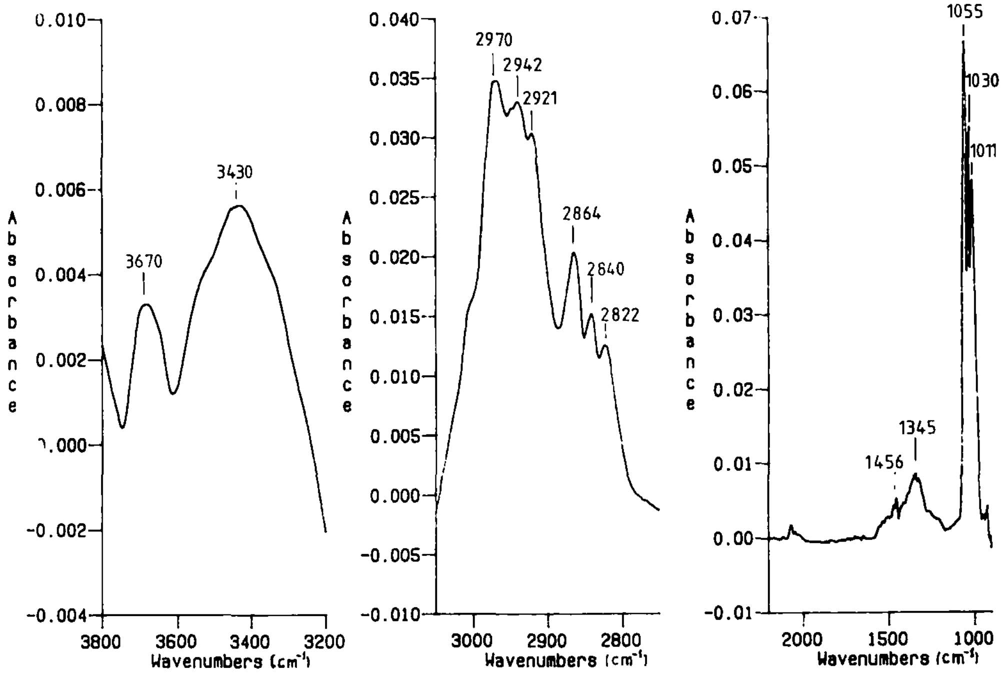


FIG. 1. Infrared spectra of gaseous CH_3OH (1 Torr) at 300 K.

TABLE 1

Characteristic Absorption Bands (in cm − ^{1}) for Gaseous and Adsorbed Methanol and Their Assignments

Assignment	$CH_3OH_{(g)}$[a]	$CH_3OH_{(g)}$[b]	CH_3OH on Pd/SiO_2 at 213 K[b]
$\nu(OH)$	3681	3670	—
		2970 (P)	
$\nu_{as}(CH_3)$	3000	2942 (Q)	2956
		2921 (R)	
		2864 (P)	
$\nu_s(CH_3)$	2844	2840 (Q)	2846
		2822 (R)	
$\delta_{as}(CH_3)$	1477	1474	1474
$\delta_s(CH_3)$	1455	1456	1451
$\delta(OH)$ in plane	1345	1345	1345
		1055 (P)	
$\nu(C-O)$	1033	1030 (Q)	—
		1011 (R)	

[a] Ref. (15).
[b] This work.

applied in this series of experiments. In contrast, the 1715 cm^{-1} band had already vanished at 213 K (Fig. 3).

High-temperature adsorption. In a subsequent experiment, the Pd/SiO_2 sample was kept in CH_3OH (1 Torr) at high temperatures, 300–523 K, and the FTIR spectra were registered *in situ* at the adsorption temperatures (Fig. 4). In this temperature range, the absorption bands at 1800–1900 cm^{-1} were the dominant spectral features. Their intensities gradually increased with increase of the adsorption time and temperature up to 373 K.

It is interesting to note that, besides the bands due to adsorbed intact CH_3OH (2955 and 2846 cm^{-1}), new bands at 2998, 2921, and 2860 cm^{-1} developed in the C–H stretching region. From 333 K, the intensity of the 2846 cm^{-1} band decreased, while that of the 2860 cm^{-1} band increased with elevation of the temperature. At and above 423 K, only the band at 2860 cm^{-1} could be observed. This band (together with the 2955 cm^{-1} band) was stable against high-temperature evacuation. The band at 1715 cm^{-1}, the intensity of which increased with time, could be clearly distinguished at 300 K, but at higher temperatures it was absent from the spectra.

3.2. Adsorption of Methanol on Potassium-Doped Pd/SiO$_2$

The adsorption of CH_3OH on 10% Pd + 2.5% K/SiO_2 at 213 K caused the appearance of the same main bands (with somewhat lower intensities) as in the case of potassium-free Pd/SiO_2 (Fig. 5). When the adsorbed layer was heated under continuous evacuation, however, the spectral changes differed considerably from those observed for Pd/SiO_2. In the C–H region, a split of the 2845 cm^{-1} band was already registered at 213 K; this doublet was stable up to 273 K. The band at 1715 cm^{-1}, which was eliminated even by evacuation at 213 K in the case of Pd/SiO_2, was much more intense and stable: it disappeared

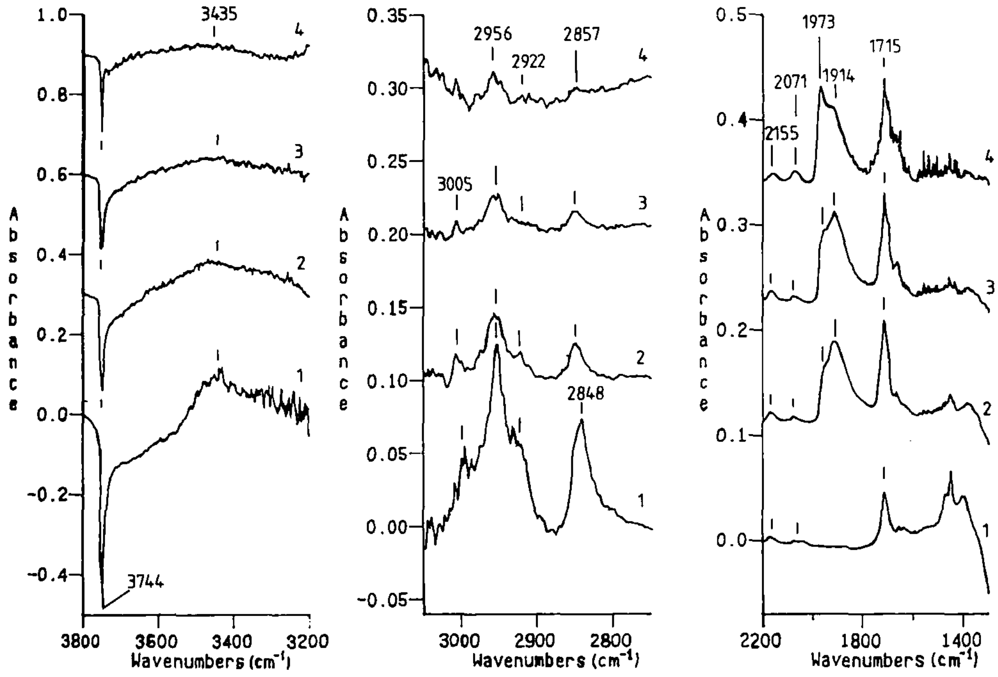


FIG. 2. Infrared spectra of 10% Pd/SiO_2 in CH_3OH (1 Torr) taken at (1) 213 K; (2) 253 K; (3) 273 K and (4) 293 K.

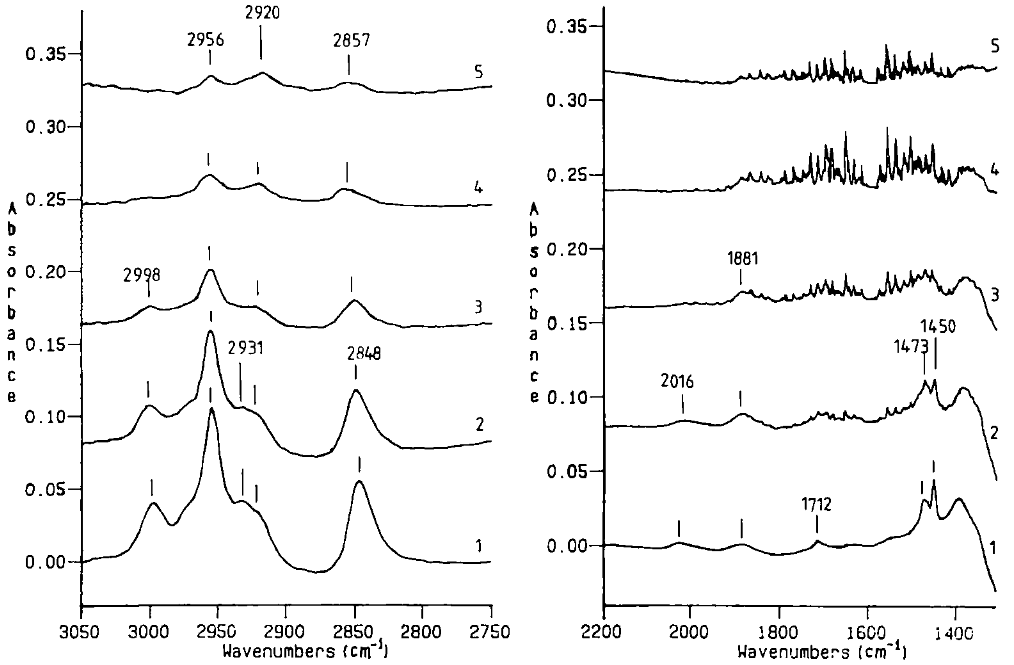


FIG. 3. Effect of evacuation on the infrared spectra of CH_3OH adsorbed on 10% Pd/SiO_2: (1) 213 K; (2) 233 K; (3) 253 K; (4) 273 K; (5) 293 K.

only at or above 273 K. One of the most striking features was the nearly total absence of the bands at 1900–1980 cm^{-1}. Weak bands were observed at 2051–2065 cm^{-1}; the latter became more intense only after the disappearance of the 1715 cm^{-1} band (Fig. 5).

3.3. Adsorption of Methanol on Pure and Potassium-Doped SiO$_2$

Adsorption of CH_3OH on the silica support (Cabosil) alone produced apparently the same absorption bands in

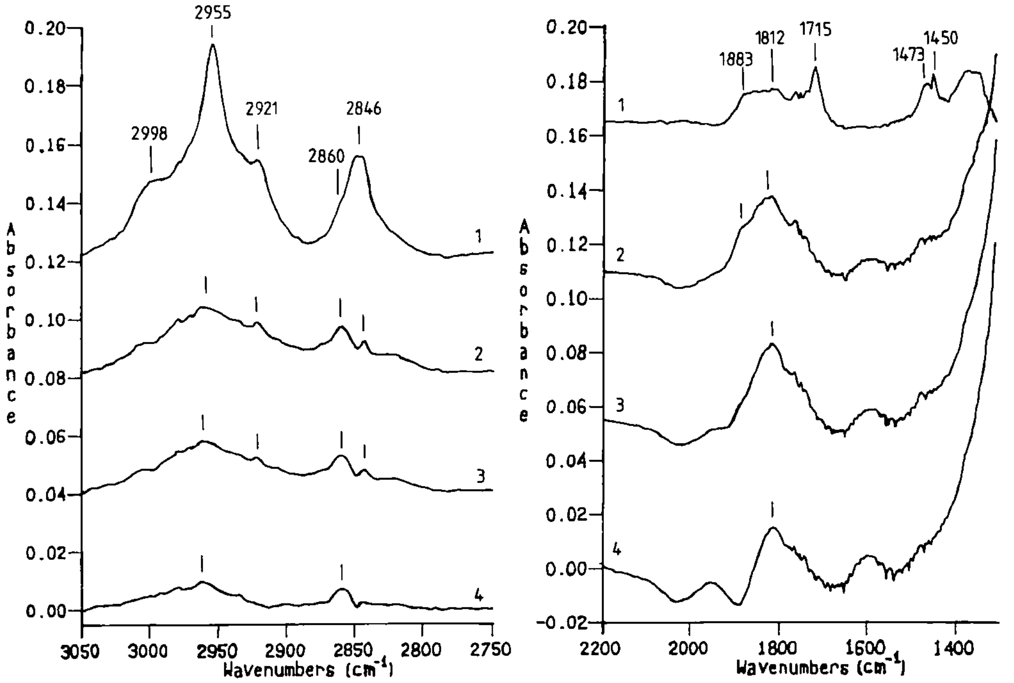


FIG. 4. Infrared spectra of 10% Pd/SiO_2 in CH_3OH (1 Torr) taken at (1) 300 K; (2) 373 K; (3) 398 K; (4) 423 K.

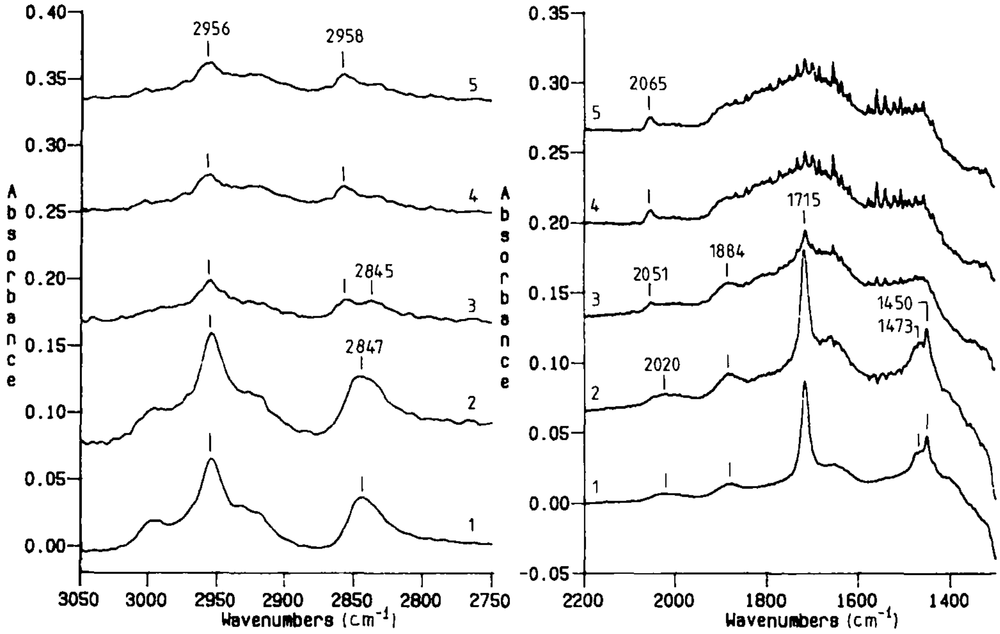


FIG. 5. Infrared spectra of 2.5% K + 10% Pd/SiO_2 in CH_3OH (1 Torr) at 213 K (1), and after subsequent evacuation at (2) 213 K, (3) 253 K, (4) 273 K, and (5) 293 K.

the C–H stretching region as for Pd/SiO_2 (Fig. 6A). The intensities of these bands on pure SiO_2, however, were somewhat lower. As regards the stability of these bands during continuous evacuation, we can say that traces of these bands could still be observed at high temperatures; they could not be eliminated even at 673 K. The band at 2846 cm^{-1} shifted to 2858 cm^{-1} at 253 K. The changes in the OH region of the SiO_2 spectra following CH_3OH ad-

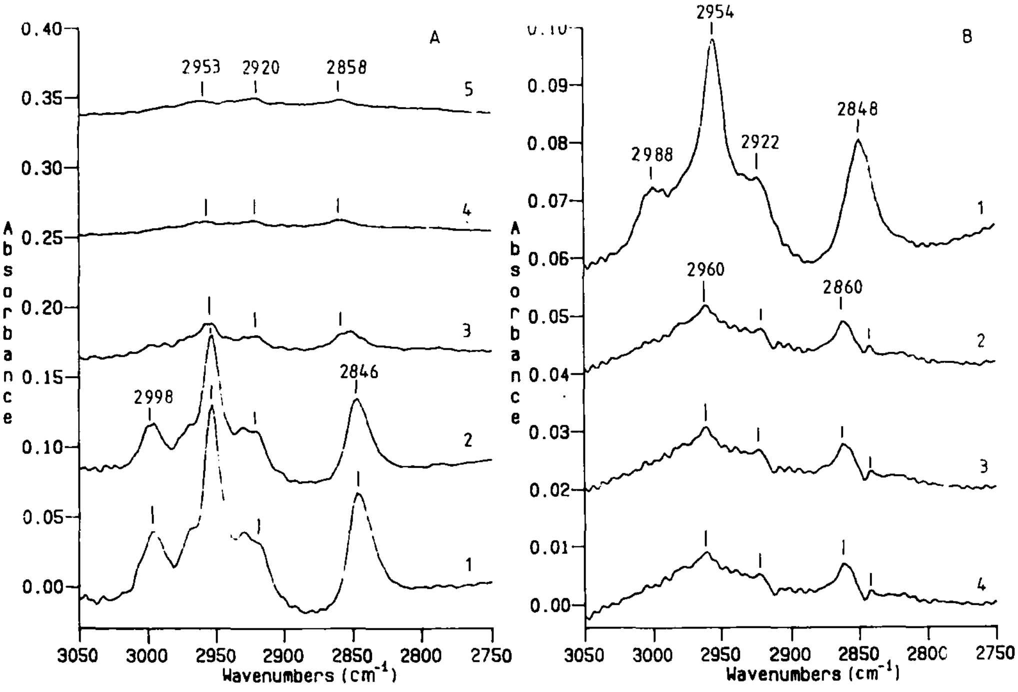


FIG. 6. (A) Infrared spectra of SiO_2 in CH_3OH (1 Torr) at 213 K (1), and after subsequent evacuation at (2) 213 K, (3) 253 K, (4) 273 K, and (5) 293 K. (B) Infrared spectra of SiO_2 in CH_3OH (1 Torr) at (1) 300 K, (2) 373 K, (3) 398 K, and (4) 423 K.

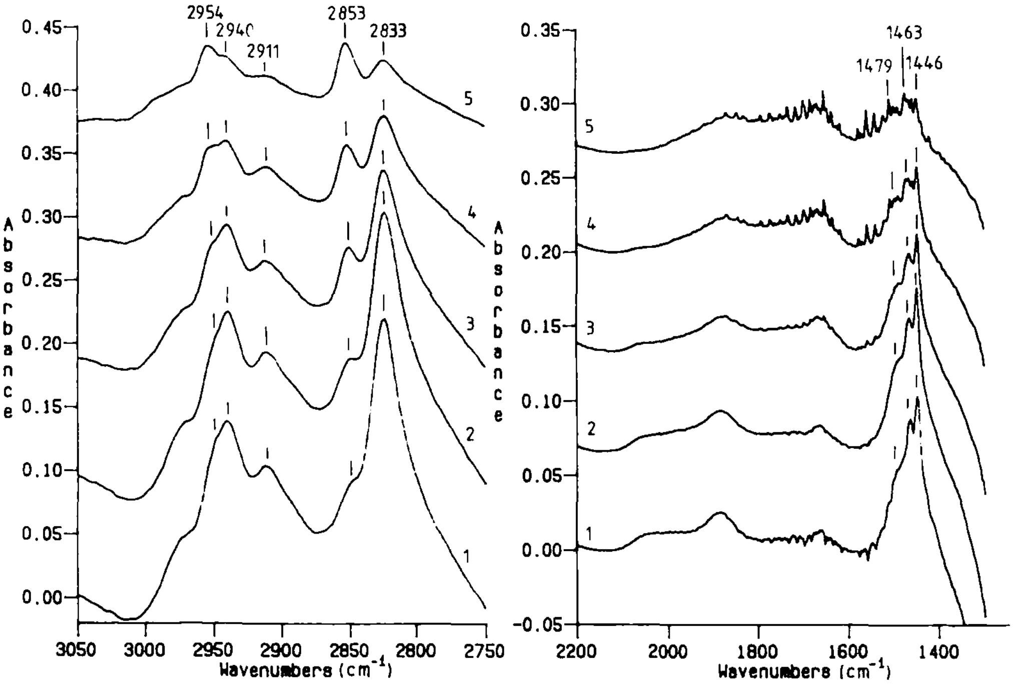


FIG. 7. Infrared spectra of 2.5% K/SiO$_2$ in CH$_3$OH (1 Torr) at 213 K (1) and after subsequent evacuation at (2) 213 K, (3) 253 K, (4) 273 K, and (5) 293 K.

sorption were the same as in the case of Pd/SiO$_2$. The same spectral features were observed on the Aerosil SiO$_2$ sample. The basic difference between the spectra for Pd/SiO$_2$ and SiO$_2$ is that for the Pd-free sample no absorption bands were registered in the range 1700–2200 cm^{-1}. Keeping the SiO$_2$ sample in CH$_3$OH at higher temperatures (300–423 K), we obtained similar results: at 300 K the bands at 2998, 2954, 2922, and 2848 cm^{-1} appeared in the C–H stretching region. At and above 373 K, however, only two bands at 2960 and 2860 cm^{-1} were observed (Fig. 6B).

The adsorption of CH$_3$OH on K-promoted SiO$_2$ catalysts produced much more intense and stable absorption bands than on K-free SiO$_2$. The C–H stretching bands appeared at somewhat lower wavenumbers, 2940 and 2833 cm^{-1} (Fig. 7). The bands at 2954 and 2853 cm^{-1} were shoulders at this temperature. The 2940 and 2833 cm^{-1} bands decreased in intensity when the adsorbed layer was heated under evacuation. All the bands in the C–H stretching region were observed at the highest temperature applied (293 K), but the dominant bands were registered at 2954 and 2853 cm^{-1} (Fig. 7). Absorption bands at 1700–2200 cm^{-1} were not observed for this sample, either. Characteristic IR absorption bands of adsorbed methanol and methoxy on the silica samples are listed in Table 2.

TABLE 2

Characteristic Absorption Bands (in cm^{-1}) of CH$_3$O$_{(a)}$ on Different Catalysts, and Their Assignments

Assignment	Pd/SiO$_2$	SiO$_2$	Pd + K/SiO$_2$	K/SiO$_2$
ν_{as}(CH$_3$)	2956	2954	2954	2954
ν_s(CH$_3$)	2857	2858	2853	2853
δ(CH$_3$)	1450	1450	1463	1447

3.4. *Adsorption of Methanol on Alumina and Alumina-Supported Pd*

Similar measurements were performed on alumina-supported samples. In this case, it was possible to detect the low-frequency bands in the region 1300–1000 cm^{-1}. Some characteristic spectra are shown in Fig. 8. Following the adsorption of CH$_3$OH on Pd/Al$_2$O$_3$ and Al$_2$O$_3$ at 213 K, we found intense absorption bands at 2943, 2823, 1666–1600, 1469, 1471, 1387, 1186, 1095, and 1035 cm^{-1}. As for SiO$_2$, the deposition of palladium on Al$_2$O$_3$ did not exert appreciable changes on the characteristics of the IR spectra of adsorbed methanol at 213–423 K, and during annealing of the adsorbed layer. The same held for the K-doped samples. The positions of the absorption bands in the C–H stretching region did not change with temperature rise. They could be eliminated only at high temperatures. A new absorption band appeared at around 1888 cm^{-1} for Pd/Al$_2$O$_3$ above 223 K, the intensity of which increased up to 423 K. It is interesting that the strong

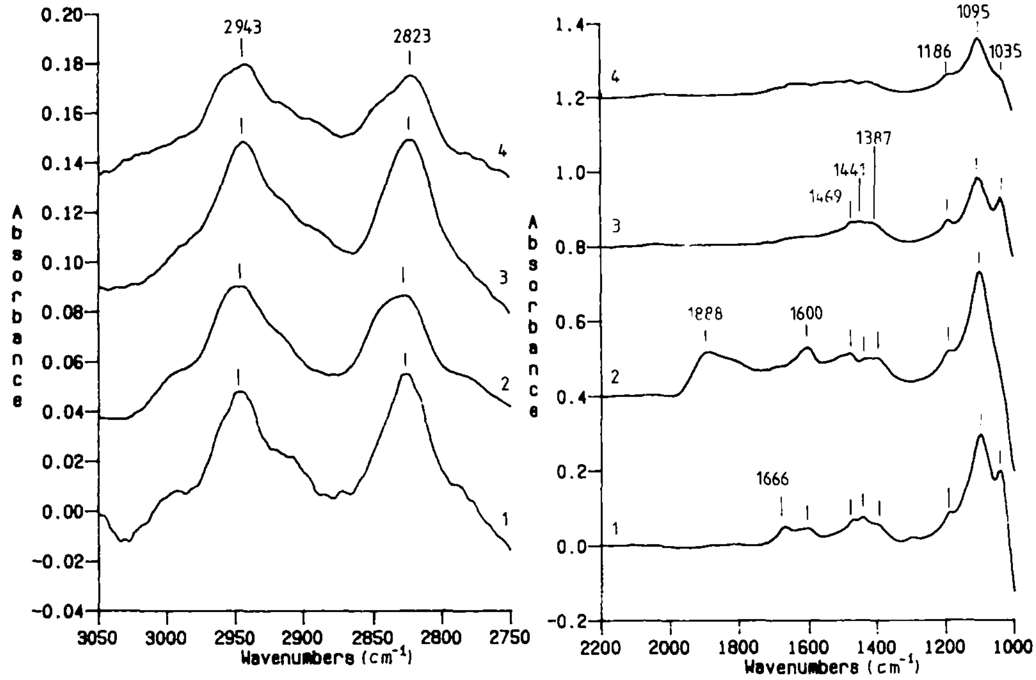


FIG. 8. Some characteristic infrared spectra following adsorption of CH_3OH (1 Torr) on 10% Pd/Al_2O_3 and 5% K + 10% Pd/Al_2O_3: (1) evacuation at 213 K after CH_3OH adsorption at 213 K on Pd/Al_2O_3; (2) evacuation at 293 K on Pd/Al_2O_3; (3) evacuation at 213 K after CH_3OH adsorption at 213 K on Pd + K/Al_2O_3; and (4) evacuation at 293 K on Pd + K/Al_2O_3.

absorption band at 1715 cm^{-1} observed for Pd/SiO_2 at 213–253 K was completely missing for Pd/Al_2O_3.

3.5. *Mass Spectrometric Analysis*

In order to determine the catalytic effect of Pd/SiO_2 samples and the products produced, mass spectrometric analysis was performed (Fig. 9). In the case of Pd/SiO_2, the evolution of gaseous products started at 423 K. The major products were CO and H_2, but CH_4, H_2O, and a compound with mass number 44, tentatively assigned as acetaldehyde, was also detected. On K-doped Pd/SiO_2, the decomposition began at somewhat higher temperatures, and occurred more slowly. Smaller amounts of

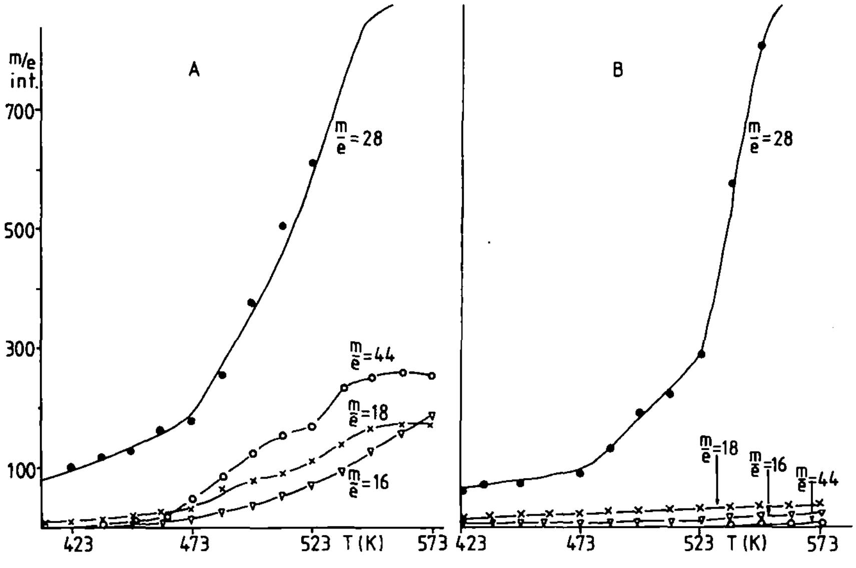


FIG. 9. Mass spectrometric analysis of the products of CH_3OH decomposition on (A) Pd/SiO_2 and (B) Pd + K/SiO_2 catalysts.

H_2O and CH_4 were formed. On Pd-free silica only negligible decomposition was observed above 573 K.

4. DISCUSSION

4.1. Literature Survey

Before discussing the results obtained, we briefly summarize the main IR spectroscopic features of CH_3OH adsorption on a silica support, on Pd metal, and on supported metals.

The interaction of CH_3OH with a silica surface has been the subject of a number of papers (16–22). When silica discs were treated with CH_3OH in an autoclave at 300–523 K for 20 h (20), methylated silicas were produced, which gave IR bands at 2958 and 2858 cm^{-1} assigned to Si–OCH_3 species. The formation of a CH_3O species on silica has also been observed under milder conditions (adsorption of 80 Torr of CH_3OH at room temperature for 2 h) (18). Identification was based on the appearance of absorption bands at 2960 and 2858 cm^{-1}, attributed to $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ of Si–OCH_3, respectively (18). Another characteristic feature of Si–OCH_3 is its high stability: it could be eliminated only by high-temperature (923–1023 K) degassing (18). In all these cases, silica was preheated to 973–1173 K in order to produce only isolated noninteracting SiOH groups.

The adsorption of CH_3OH has also been investigated on different faces of Pd single crystals by electron spectroscopy and high-resolution electron energy loss spectroscopy (4–14). Christmann and Demuth (4) first observed the formation of methoxy on the Pd(100) surface. Four different methoxy species have been identified; the most stable one existed even above 300 K. The formation of methoxy has been also identified on the Pd(111) surface by HREELS (7). Loss features at 3015, 2865, 1430/1375, 1140, 1005, and 325 cm^{-1} were attributed to adsorbed methoxy (7). These peaks developed at 170 K and disappeared at 240 K (7). Practically the same loss features were observed for other metals (23–30). The losses due to methoxy are in general very weak; this was probably the reason Gates and Kesmodel (5) found no evidence of the formation of methoxy on the Pd(111) surface.

Whereas previous IR and HREELS studies unambiguously suggested that only rupture of the O–H bond is involved in the dissociation of CH_3OH on Pt metals, Lewis *et al.* (9) recently demonstrated the rupture of both O–H and C–O bonds in the dissociation of CH_3OH on Pd(111), which led to a controversy (10–14).

As concerns the identification of methoxy species in the dissociation of methanol on supported metals, we have found only a few papers (31, 32). The appearance of absorption bands at 2930–2958, 2820–2857, and 1050–1065 cm^{-1} following the adsorption of CH_3OH on Rh/SiO_2, Rh–Ce/SiO_2 (31), and Pd/ZrO_2 (32) was considered to be evidence for CH_3O production on the supports. To the best of our knowledge, the adsorption of CH_3OH on Pd/SiO_2 catalysts has not previously been investigated by IR spectroscopy.

4.2. Adsorption and Dissociation of Methanol on SiO_2

The obtained IR spectrum of gaseous CH_3OH agrees well with that reported in the literature (15) (Fig. 1). In the presence of silica at 213 K, the characteristics of the IR spectrum are basically changed. Sharp absorption bands are observed at 2956 and 2846 cm^{-1}, which we ascribe to the vibrations of molecularly adsorbed CH_3OH. Assignments are shown in Table 2. The adsorption very probably involves strong hydrogen bonding between CH_3OH and the surface OH groups on the silica, manifested in the development of a broad absorption centered at around 3435 cm^{-1} and in the negatively going feature at 3744 cm^{-1}.

When the adsorbed layer was annealed to 253 K, the band at 2846 cm^{-1} ($\nu_s(CH_3)$ in intact methanol) for silica shifted to 2858 cm^{-1} (Fig. 6). At the same time, the broad band centered at 3435 cm^{-1} disappeared, very probably because of the desorption of molecular CH_3OH from the surface.

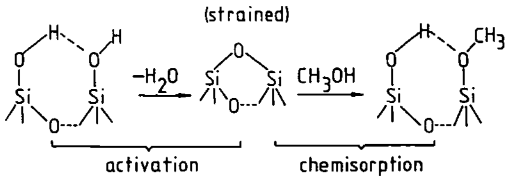
In the high-temperature (300–573 K) adsorption of CH_3OH on SiO_2, besides the 2846 cm^{-1} band attributed to $\nu_s(CH_3)$ in molecularly adsorbed methanol, a new band developed at 2860 cm^{-1}. This band became more intense, while the 2846 cm^{-1} band vanished with temperature rise.

As the absorption band at 2956 and 2857–2860 cm^{-1} exhibited a high thermal stability (it could not be eliminated even at 673 K), it cannot originate from molecularly adsorbed methanol. We believe that these bands are due to the formation of methoxy, and that they can be assigned to $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ in $CH_3O_{(a)}$ (18). Accordingly, the interaction between Si–OH and CH_3OH can occur to a small extent even at around 250 K to yield surface Si–OCH_3 species.

As regards the methylation of silica, there are two basic routes. In the first (16), the esterification of surface OH occurs:

$$\text{Si–O–H} + CH_3OH \rightarrow \text{Si–O–}CH_3 + H_2O \qquad [1]$$

The second proceeds according to the reaction



[2]

This is based on the finding that the irreversible adsorption of methanol on silica occurs to a greater extent, the higher the temperature at which the silica was degassed, i.e., the lower the surface OH content (17). Borello *et al.* (18) concluded that siloxane bridges are reactive only when they are formed at temperatures higher than 623 K. As we degassed our samples at 673 K, and detected the formation of $SiOCH_3$ even at around 250 K, we may speculate that in this case the second route is the dominant step (Eq. 2). This is certainly true for samples degassed at 873–973 K, when more intense absorption bands due to $Si{-}OCH_3$ are produced.

4.3. Adsorption and Dissociation of Methanol on Pd/SiO$_2$

The adsorption of methanol on Pd/SiO_2 at 213 K apparently led to the same spectral features as for pure silica (compare Figs. 2, 4, and 6). A change in the position of the 2848 cm^{-1} band to 2857 cm^{-1} also occurred at 253 K. The only other difference was that the relative intensity of the absorption band at 2920 cm^{-1} was clearly higher. The behaviour was the same when CH_3OH was adsorbed at 300–423 K. This result suggests that the presence of Pd contributes only slightly, if at all, to the absorption of molecularly and dissociatively adsorbed methanol detected by IR on the silica support.

In order to establish minor differences between the IR spectra of CH_3OH adsorbed on Pd/SiO_2 and SiO_2 samples, we subtracted the spectra registered for SiO_2 from those measured for Pd/SiO_2 under exactly the same experimental conditions. Magnified difference spectra are shown in Fig. 10. In the region of the C–H stretching frequency, intense absorption bands remain at 2954 and 2844 cm^{-1} in the spectra at 223 K, which we may attribute to the vibrations of adsorbed CH_3OH. The intensities of these bands decrease to very low values even during heating of the adsorbed layer under continuous evacuation to 243–253 K. The shape of the weak, broad band between 2820 and 2870 cm^{-1} suggests that it may contain a feature at 2857 cm^{-1} due to methoxy species ($\nu_s(CH_3)$). If we accept that the deposition of 10% Pd (the dispersion is only 5.3%) does not change the adsorptive properties of the free silica (its surface area is about 200 m^2/g), we may associate these bands with the adsorbed species bonded to Pd crystallites. The fact that the intensities of these bands are considerably reduced at 273–293 K supports this conclusion, as both CH_3OH and CH_3O chemisorbed on Pd are much less stable than on the silica surface.

The relative increase in the absorption band at 2920 cm^{-1} at 273–293 K, observed in Figs. 3 and 9, requires special discussion. A weak band around this wavenumber also appeared for pure silica, which was assigned to a combination band (21). However, this assignment for the significant enhancement of this band at 253–293 K cannot be applied in the present case, if the slight changes in the other spectral regions are taken into account. Therefore, we incline to think that this band is due to an adsorbed $CH_3(a)$ species formed by cleavage of the C–O bond of methanol on Pd,

$$CH_3{-}OH_{(a)} = CH_{3(a)} + OH_{(a)},$$

and can be assigned to the asymmetric stretch of $CH_3(a)$. This absorption band has been detected for the same Pd/SiO_2 sample following the dissociation of CH_3I at 212–223 K (11, 33). A loss feature at around this energy in the

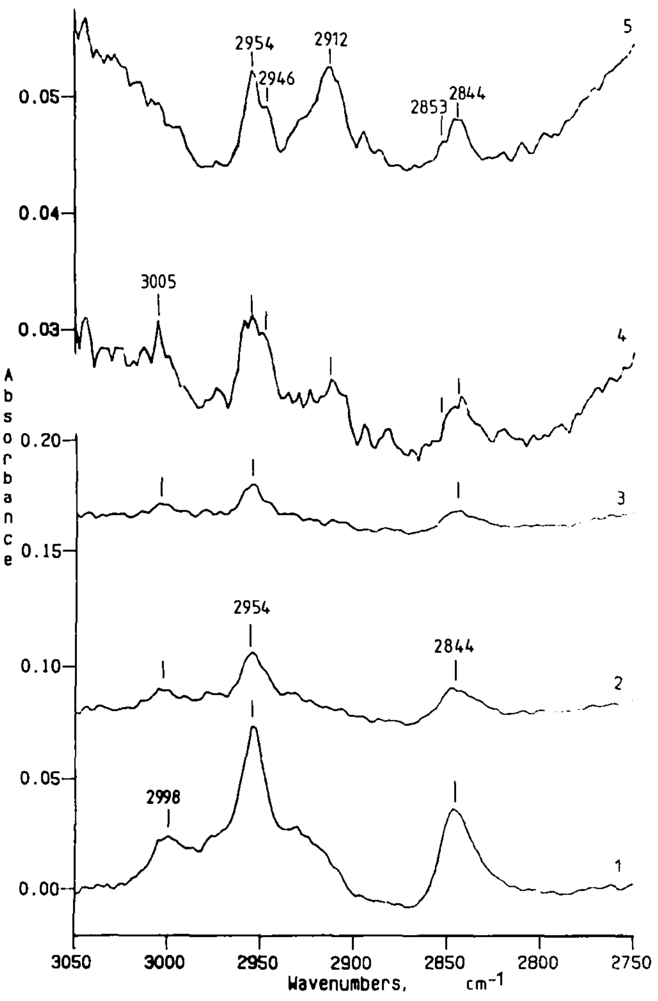


FIG. 10. Difference IR spectra obtained after CH_3OH adsorption on 10% Pd/SiO_2 and SiO_2. Spectrum registered for SiO_2 has been subtracted from each spectrum taken for Pd/SiO_2 under exactly the same conditions. Adsorption of CH_3OH was performed at 213 K, then the samples were degassed and warmed to selected temperatures under continuous evacuation: (1) 223 K, (2) 243 K, (3) 253 K, (4) 273 K, (5) 293 K.

HREELS spectra was also observed in the thermal and photoinduced dissociation of alkyl halides on Pt(111) and Ru(001) surfaces, and was also attributed to the $\nu_a(CH_3)$ vibration (34, 35).

As this dissociation route of CH$_3$OH has been claimed to occur on Pd(111) (9, 13), but not on the Pd(100) surface (11, 12), we may conclude that the dissociation of methanol is a structure-sensitive process. On polycrystalline Pd deposited on silica, both pathways of methanol dissociation, (viz. rupture of the O–H and C–O bonds), respectively, proceed. Detailed analysis of the spectra suggests that the 2920 cm^{-1} absorption band ascribed to adsorbed CH$_3$ can be detected up to about 330–350 K. This temperature lies between the temperatures of CH$_3$ elimination on Pd(111) (450 K) and Pd(100) (300 K), determined under UHV conditions.

Additionally, several absorption bands (strong ones at 1715, 1914, and 1964 cm^{-1}, and weaker ones at 2078 and 2165 cm^{-1}) not observed on silica were detected on Pd/SiO$_2$, which clearly indicates that CH$_3$OH interacts with Pd to yield various adsorbed species. The band at 1715 cm^{-1} appeared even at 213 K; its intensity increased up to 253 K, and then remained practically constant up to 293 K. The other bands developed at 233 K and intensified at higher temperatures (Fig. 2). These bands exhibited high thermal stability; they could be eliminated only by degassing at 573 K. An exception was the band at 1715 cm^{-1}, which disappeared even on evacuation at 253 K (Fig. 3).

The difference in thermal stability of the absorption bands clearly suggests that they are due to different adsorbed species. As to the positions of the high-frequency bands above 1800 cm^{-1}, and their thermal behaviour, we can conclude that these bands are those of adsorbed CO formed in the surface reaction. In agreement with the literature data (36–38), we assign the band at 1880–2000 cm^{-1} to twofold coordinated CO, and the band at 1800–1880 cm^{-1} band to threefold coordinated CO on Pd. The band at 2000–2120 cm^{-1} is due to single-coordinated (or on-top) CO.

In order to establish the nature of the species responsible for the 1715 cm^{-1} band, HCHO and CH$_3$CHO were separately adsorbed on Pd/SiO$_2$ at 213–223 K (Fig. 11). HCHO adsorption caused the appearance of the absorption band at 1725 cm^{-1}, assigned to $\nu(CO)\eta^2$-formaldehyde, while the adsorption of CH$_3$CHO led to the bands at 1714 cm^{-1}, attributed to $\nu(CO)\eta^2$-acetaldehyde (39, 40). Degassing of the sample caused attenuation of the absorption bands of both aldehydes at 213 K. The band observed at 1724 cm^{-1} on HCHO adsorption completely disappeared on evacuation at 223 K. The 1714 cm^{-1} band registered on CH$_3$CHO adsorption, however, was stable against evacuation up to 253 K. In addition we observed in both cases intense absorption bands due to adsorbed

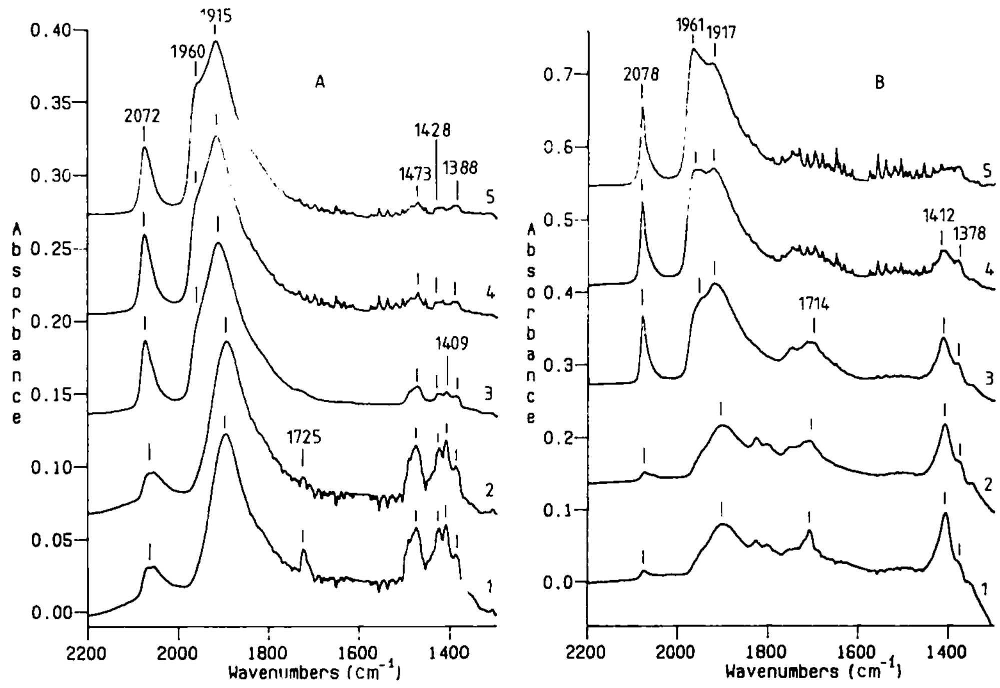


FIG. 11. Infrared spectra of 10% Pd/SiO$_2$ in the presence of HCHO (1 Torr) (A) and CH$_3$CHO (0.1 Torr) (B) at 213 K (1) and after subsequent evacuation at 213 K (2), 253 K (3), 273 K (4), and 293 K (5).

CO formed in the decomposition of aldehydes. These features lead us to believe that the 1715 cm^{-1} band detected in the adsorption of CH_3OH can be attributed to the $\nu(CO)\eta^2$-acetaldehyde vibration of acetaldehyde formed on the Pd surface. The decomposition of acetaldehyde on palladium could also contribute to the formation of adsorbed CO. An alternative explanation is that the 1715 cm^{-1} band is due to multilayered adsorbed acetaldehyde (41). This, however, is not likely, as the 1715 cm^{-1} band was detected on the K-dosed sample even at 253 K, where we cannot count on the existence of a multilayer acetaldehyde.

Both adsorbed formaldehyde (32) and adsorbed acetaldehyde (7) have formerly been assumed as surface intermediates in the catalytic decomposition of methanol on Pd surfaces. We detected a band at 3005 cm^{-1}, which is probably due to $\nu(CH_4)$ (32).

4.4. Effects of Potassium on the Dissociation Pathways of Methanol

In the case of Rh(111) (42) and Pd(100) (11) surfaces, we found that potassium adatoms increased the binding energy of adsorbed CH_3OH, and enhanced the extent of cleavage of the methanolic O–H bond. Above a monolayer of potassium (when potassium exhibits mainly a metallic character), the potassium interacted directly with CH_3OH to give $K{-}OCH_3$ as a surface compound. This surface species exhibited a high thermal stability; its complete decomposition was achieved only at 450–500 K (11, 42).

In the present case, the addition of potassium to silica significantly enhanced the intensities of the absorption bands due to molecularly adsorbed methanol, which exhibited higher stability than that observed on potassium-free silica. The absorption bands attributed to methoxy species at 2957 and 2853 cm^{-1} were also more intense. The same feature was observed for K-dosed Pd/SiO_2. The formation of the $CH_3(a)$ species, however, was not appreciably altered. Potassium additive also exerted an influence on the reactions assumed to occur on the Pd surface. This comprised the following features: (i) the stability of the 1715 cm^{-1} band due to the $\nu(C{-}O)\eta^2$-aldehyde vibration of acetaldehyde was greatly increased, and (ii) lower amounts of CO were detected by both low-temperature IR spectroscopic measurements and high-temperature MS analysis.

In the interpretation of these features, we may assume that potassium oxide or hydroxide is more reactive than the Si–OH or siloxane groups. As a result, methanol reacts with potassium oxide to yield the $K{-}OCH_3$ species, which, in accord with our previous findings on single-crystal surfaces (11, 42), decomposes much more slowly. The stabilization of acetaldehyde by potassium could also contribute to the limited formation of CO.

4.5. The Behaviour of Alumina Samples

We observed similar features when the silica support was replaced by alumina. In harmony with previous observations (43), methanol dissociates easily on alumina, and the occurrence of this process can be established by registering the spectra in the low-frequency region, 1000–1100 cm^{-1}. The absorption band at 1095 cm^{-1} due to $\nu(CO)$ in $CH_3O(a)$ appeared even at the lowest temperature, 213 K, for pure and Pd-containing samples, and increased in intensity with temperature rise.

It appeared that addition of potassium to the samples stabilized the adsorbed species formed, but did not induce a new pathway of methanol dissociation. A striking difference between silica and alumina-supported Pd is that in the latter case there was no absorption band at 1720–1700 cm^{-1}, attributed to $\nu(CO)\eta^2$-acetaldehyde.

5. CONCLUSIONS

(i) Methanol interacts with the OH groups of silica even at 213 K, and reacts with the siloxane bridges above 253 K to produce very stable $Si{-}O{-}CH_3$ species.

(ii) The deposition of palladium on the silica surface only slightly influences the processes occurring on silica. The dissociation of methanol via both O–H and C–O bond breaking is observed on Pd.

(iii) Adsorbed methanol, very probably via methoxy formation, decomposes easily on Pd even at 233 K, to give CO two- and threefold coordinated to Pd. Weakly adsorbed acetaldehyde is also observed at 213 K.

(iv) Potassium additive strongly interacts with methanol, very probably through the formation of stable surface $K{-}OCH_3$.

ACKNOWLEDGMENTS

The authors express their thanks to Dr. T. Bánsági for carrying out mass spectrometric analysis. A loan of $PdCl_2$ from Johnson–Matthey PLC is gratefully acknowledged.

REFERENCES

1. Poutsma, M. L., Elek, L. F., Ibarbia, P. A., Risch, A. P., and Rabo, J. A., *J. Catal.* **52,** 157 (1978); Fajula, F., Anthony, R. G., and Lunsford, J. H., *J. Catal.* **73,** 237 (1982); Rieck, J. S., and Bell, A. T., *J. Catal.* **91,** 104 (1985).
2. Ramaroson, E., Kieffer, R., and Kiennemann, A., *J. Chem. Soc. Chem. Commun.*, 645 (1982); Erdöhelyi, A., Pásztor, M., and Solymosi, F., *J. Catal.* **98,** 166 (1986).
3. Poels, E. K., and Ponec, V., *in* "Catalysis," Specialist Periodical Report, Vol. 6, p. 196. Royal Society of Chemistry, 1983.

4. Christmann, K., and Demuth, J. E., *J. Chem. Phys.* **76,** 6308 and 6318 (1982).
5. Gates, J. A., and Kesmodel, L. L., *J. Catal.* **83,** 437 (1983).
6. Davis, J. L., and Barteau, M. A., *Surf. Sci.* **197,** 123 (1988); Davis, J. L., and Barteau, M. A., *Surf. Sci.* **187,** 387 (1987).
7. Davis, J. L., and Barteau, M. A., *Surf. Sci.* **235,** 235 (1990).
8. Bhattacharya, A. K., Chesters, M. A., Pemble, M. E., and Sheppard, N., *Surf. Sci.* **206,** L845 (1988).
9. Levis, R. J., Zhicheng, J., and Winograd, N., *J. Am. Chem. Soc.* **111,** 4605 (1989).
10. Guo, X., Hanley, L., and Yates, J. T., Jr., *J. Am. Chem. Soc.* **111,** 3155 (1989).
11. Berkó, A., Raskó, J., and Solymosi, F., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi and P. Tétényi, Eds.), p. 359. Akadémiai Kiadó, Budapest, 1993. Solymosi, F., Berkó, A., and Tóth, Z., *Surf. Sci.* **285,** 197 (1993).
12. Solymosi, F., and Révész, K., *J. Am. Chem. Soc.* **113,** 9145 (1991).
13. Kruse, N., Rebholz, M., Matalin, V., Chuah, G. K., and Block, J. H., *Surf. Sci.* **238,** L457 (1990).
14. Rebholz, M., Matalin, V., Prins, R., and Kruse, N., *Surf. Sci.* **251/252,** 1117 (1991); Rebholz, M., and Kruse, N., *J. Phys. Chem.* **95,** 7745 (1991).
15. Shimanuchi, T., "Tables of Molecular Vibrational Frequencies," Consolidated Vol. I, NSRDS—Natl. Bur. Stand. No. 39. U.S. Government Printing Office, Washington, DC, 1972.
16. McDonald, A. N., *J. Phys. Chem.* **62,** 175 (1958); Kavasaki, K., Senzaki, K., and Tsuchija, I, *J. Colloid. Sci.* **19,** 144 (1964).
17. Beliakova, L. D., and Kiselev, A. V., *Dokl. Akad. Nauk SSSR* **119,** 2 (1958).
18. Borello, E., Zecchina, A., and Morterra, C., *J. Phys. Chem.* **71,** 2938 (1967); **71,** 2945 (1967).
19. Morterra, C., and Low, M. J. D., *J. Phys. Chem.* **73,** 321 (1969).
20. Kitahara, S., *Bull. Chem. Soc. Jpn.* **49,** 3389 (1976); Takezawa, N., and Kobayashi, H., *J. Catal.* **25,** 179 (1972).
21. Morrow, B. A., *J. Chem. Soc. Faraday Trans.* I **70,** 1527 (1974); Morrow, B. A., Thomson, L. W., and Wetmore, R. W., *J. Catal.* **28,** 332 (1973).
22. Kubelkova, L., Schürer, P., and Jiru, P., *Surf. Sci.* **18,** 245 (1969).
23. Sexton, B. A., *Surf. Sci.* **88,** 299 (1979).
24. Demuth, J. E., and Ibach, H., *Chem. Phys. Lett.* **60,** 395 (1979).
25. Sexton, B. A., *Surf. Sci.* **102,** 271 (1981).
26. Hrbek, J., de Paola, R. A., and Hoffman, F. M., *J. Vac. Sci. Technol.* **21,** 1222 (1983).
27. Ibach, H., and Mills, D. L., "Electron Energy Loss Spectroscopy and Surface Vibrations." Academic Press, New York, 1978.
28. Hrbek, J., de Paola, R. A., and Hoffman, F. M., *J. Chem. Phys.* **81,** 2818 (1984).
29. Parmeter, J. E., Jiang, X., and Goodman, D. W., *Surf. Sci.* **240,** 85 (1990).
30. Houtman, C., and Barteau, M. A., *Langmuir* **6,** 1558 (1990).
31. Lavalley, J. C., Saussey, J., Lamotte, J., Breault, R., Hindermann, J. P., and Kiennemann, A., *J. Phys. Chem.* **94,** 5941 (1990); Anderson, J. A., McQuire, M. W., Rochester, C. H., and Sweeney, T., *Catal. Today* **9,** 23 (1991).
32. Schild, C., and Wokaun, A., *J. Mol. Catal.* **63,** 223 (1990).
33. Raskó, J., Bontovics, J., and Solymosi, F., *J. Catal.* **143,** 138 (1993).
34. Henderson, M. A., Mitchell, G. E., and White, J. M., *Surf. Sci.* **184,** L325 (1987).
35. Zhou, Y., Anderson, M. A., Feng, W. M., and White, J. M., *Surf. Sci.* **224,** 386 (1989).
36. Bradshaw, A. M., and Hoffman, F. M., *Surf. Sci.* **72,** 513 (1978).
37. Kikuzono, Y., Kagami, S., Naito, S., Onishi, T., and Tamaru, K., *Faraday Discuss. Chem. Soc.* **72,** 135 (1981).
38. Palazov, A., Chang, C. C., and Kokes, R. J., *J. Catal.* **36,** 338 (1975).
39. Schild, C., Wokaun, A., and Baiker, A., *J. Mol. Catal.* **63,** 243 (1990); Yates, J. T., and Cavanagh, R. R., *J. Catal.* **74,** 97 (1982).
40. Henderson, M. A., Zhou, Y., and White, J. M., *J. Am. Chem. Soc.* **111,** 1185 (1989); Dai, C. H., and Worley, S. D., *Langmuir* **4,** 326 (1988).
41. McCabe, R. W., Di Maggio, C. L., and Madix, R. M., *J. Phys. Chem.* **89,** 854 (1985).
42. Berkó, A., Tarnóczy, T. I., and Solymosi, F., *J. Phys. Chem.* **88,** 6170 (1989); Solymosi, S., Berkó, A., and Tarnóczy, T. I., *J. Chem. Phys.* **87,** 6745 (1987).
43. Greenler, R. G., *J. Chem. Phys.* **37,** 2094 (1962); Busca, G., Rossi, P. F., Lorenzelli, V., Benaissa, M., Travert, J., and Lavalley, J. C., *J. Phys. Chem.* **89,** 5433 (1985).