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# Infrared Spectroscopic Study of the Adsorption and Dissociation of $CH_2Cl_2$ on $Pd/SiO_2$

## Generation of $CH_2$ Species

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**The adsorption and dissociation of $CH_2Cl_2$ have been investigated by means of infrared spectroscopy combined with mass spectrometry. $CH_2Cl_2$ adsorbs molecularly on $Pd/SiO_2$ at low temperature (193–213 K) and interacts strongly with the OH groups of silica to form H-bridge-bonded methylene halide. This is exhibited by a significant attenuation of the 3744 $cm^{-1}$ band exhibited by silica and by the development of a broad spectral feature at 3662 $cm^{-1}$. The dissociation of $CH_2Cl_2$ was observed at 233–243 K. The primary product of dissociation, $CH_2$, was characterized by absorption bands at 2984 and 2907 $cm^{-1}$. The $CH_2$ species dimerized into $C_2H_4$ above 263 K. A fraction of ethylene desorbed, while another fraction was transformed into ethylidyne. The latter compound is characterized by absorption bands at 2922 and 2857 $cm^{-1}$. By means of mass spectrometry $C_2H_4$ and HCl were identified in the desorbing gases at 250–330 K. Decomposition of $CH_2Cl_2$ occurred above 350 K yielding $C_2H_4$, $CH_4$, HCl, and $H_2O$. Some exploratory measurements were also performed with $CH_2I_2$.** © 1995 Academic Press, Inc.

## 1. INTRODUCTION

This study is a continuation of our research program aiming to produce $CH_x$ fragments on Pd catalysts. In the frame of this program we examined first the adsorption and dissociation of $CH_3X$ ($X$, halide) (1), $CH_2X_2$ (2), and $C_2H_5X$ (3) on the Pd(100) surface under UHV conditions. We found that iodine compounds are more suitable to generate $CH_x$ fragments than materials containing chloride. In addition, illumination of adsorbed layers markedly enhanced the extent of dissociation and produced $CH_x$ fragments in a larger quantity even at 85–90 K, far below the temperature of their secondary thermal reactions. As an extension of this work to actual catalysts, the adsorption of $CH_3Cl$ and $CH_3I$ was recently investigated on $Pd/SiO_2$ by Fourier transform infrared spectroscopy (FTIR), which proved to be a very sensitive tool to follow the dissociation and reactions of these compounds (4).

The present paper deals with the study of the surface interaction of $CH_2Cl_2$ with the same $Pd/SiO_2$ catalyst. For comparison, some measurements have been also carried out on the adsorption of $CH_2I_2$. The primary aim of the work is to examine the possibility of the generation of methylene, $CH_2$, species and to determine its thermal stability and reactions. It is envisioned that the results obtained provide a better understanding of the catalytic reactions involving $CH_2$ intermediates. In addition, it is hoped that the results give useful information for the catalytic destruction of halogenated hydrocarbons, which is an important task for the cleaning of the environment.

As regards the adsorption of methylene halides on supported metals, we found no data in the literature. Several works have dealt, however, with the adsorption and decomposition of these compounds on metal surfaces under UHV conditions (2, 5–10).

## 2. EXPERIMENTAL

$Pd/SiO_2$ samples were prepared by incipient wetting of silica (Cabosil) with an aqueous solution of palladium chloride (Johnson–Matthey). For preparation triply distilled water was used. The Pd content was 10 wt.%. All materials used were of analytical grade. The purity of Cabosil $SiO_2$ was checked by inductively coupled plasma (ICP) spectroscopy. The following elements were detected: Zn, 0.00128%; Ni, 0.00076%; Fe, 0.00053%; and Co, 0.00002%. Tests for Mg, Al, Ca, Cr, Ba, Ti, Na, K, Li, Cu, and Cd were negative. After impregnation the samples were dried in air at 373 K. For IR studies the dried $Pd/SiO_2$ powder was pressed into self-supporting wafers (30 × 10 mm, 10 $mg/cm^2$). The pretreatments of the samples were performed in a vacuum IR cell and agreed with that applied in our previous work (4). Briefly, the samples were (a) heated (20 K/min) to 673 K under

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continuous evacuation, (b) oxidized with 100 Torr of $O_2$ (133.3 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 temperature is sufficient to achieve a complete reduction. This was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment.

$CH_2Cl_2$ (Merck) and $CH_2I_2$ (Merck) were purified by fractional distillation and stored in a glass bulb. $CH_2I_2$ was protected against light.

Infrared spectra were recorded with a BIORAD (Digilab) FTIR spectrometer (FTS 7) with a wavenumber accuracy of ±2 $cm^{-1}$. Typically 16 scans were registered. All subtractions of the spectra were taken without the use of a scaling factor ($f$ = 1.0000). Mass spectrometric analysis was performed with the help of an MS 10 (AEI) mass spectrometer.

## 3. RESULTS

### *3.1. Adsorption of $CH_2Cl_2$*

Figure 1 shows the infrared spectrum of gaseous $CH_2Cl_2$ (10 Torr). Absorption bands are listed in Table 1, where the literature data are also presented. Our gas-phase spectrum is consistent with that obtained formerly for $CH_2Cl_2$ gas (11, 12).

The spectrum obtained in the presence of 10% Pd/$SiO_2$ at 213 K showed spectral features different from those of the $CH_2Cl_2$ gas spectrum registered at 300 K. The band at 3004 $cm^{-1}$ did not appear, but a new band at 3064 $cm^{-1}$ could be detected. A small shift of −2 $cm^{-1}$ in the position of $\nu_s(CH_2)$ occurred, and a very weak band at 2907 $cm^{-1}$ also appeared. More interestingly, a greater shift in the ($CH_2$) deformation mode (1464 $cm^{-1}$) ($\Delta\nu$ = −38 $cm^{-1}$) was observed on the spectrum of adsorbed $CH_2Cl_2$ (Fig. 1). In response to $CH_2Cl_2$ adsorption the intensity of the silica OH band at 3744 $cm^{-1}$ decreased and a broad band centered at 3662 $cm^{-1}$ developed. Evacuation at 213 K caused only a slight attenuation of the absorption bands observed in the presence of gaseous $CH_2Cl_2$.

Heating of the sample in vacuum to 243 K led to the complete elimination of the 3064 $cm^{-1}$ band (Fig. 2). Further heating of the sample under continuous evacuation to 263 K resulted in a small diminution of the 2984 and 2907 $cm^{-1}$ bands (Fig. 2). At and above 263 K new bands at 2922 and 2857 $cm^{-1}$ developed with the concomitant decrease of the bands at 2984 and 2907 $cm^{-1}$. Maximum intensities of the new bands were measured at 373 K, and the bands at 2984, 2922, and 2857 $cm^{-1}$ were detected up to 473 K.

Mass-spectrometric analysis of the gas phase during heating of the adsorbed layer showed the desorption of $CH_2Cl_2$ above 230 K. A slight decomposition of $CH_2Cl_2$ also occurred as indicated by the formation of $C_2H_4$ and HCl (Fig. 3A).

In subsequent measurements the Pd/$SiO_2$ sample was slowly heated in $CH_2Cl_2$ vapor from 133 to 293 K and the

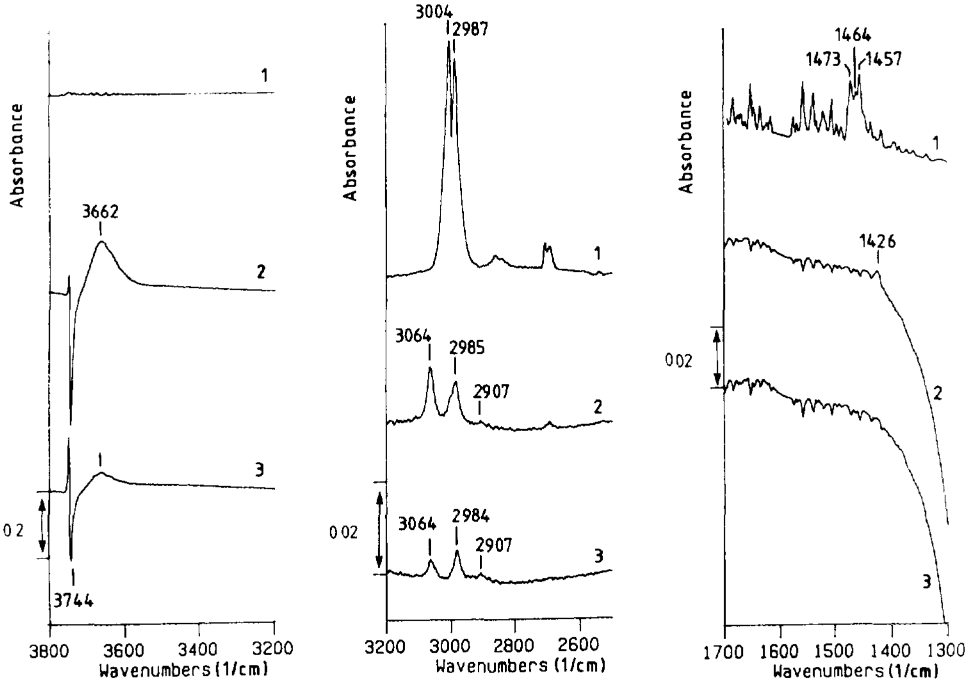


FIG. 1. Spectra of Pd/$SiO_2$ following the adsorption of 10 Torr $CH_2Cl_2$ at 213 K and subsequent evacuation. For comparison the gas-phase spectrum of $CH_2Cl_2$ is also shown. 1, $CH_2Cl_2$ gas at 300 K; 2, Pd/$SiO_2$ in the presence of $CH_2Cl_2$ at 213 K; 3, evacuation at 213 K after (2).

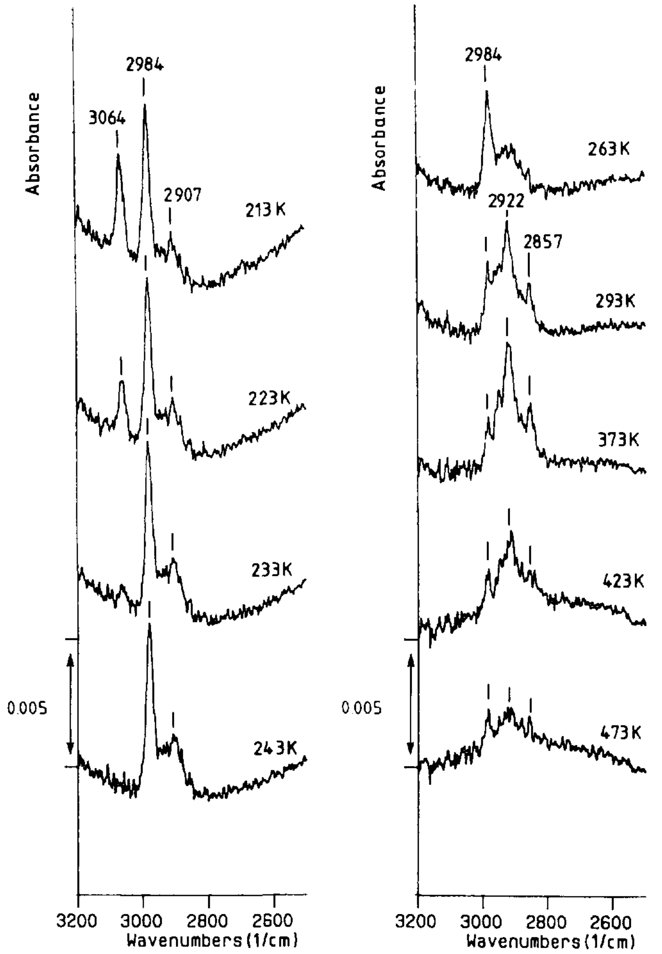


FIG. 2. Spectral changes observed on heating the adsorbed layer on Pd/$SiO_2$ under continuous evacuation. $CH_2Cl_2$ (10 Torr) was adsorbed at 213 K.

spectra were registered at selected temperatures. With the increase of temperature, a significant change occurred in the OH frequency range: the new band at 3597–3660 $cm^{-1}$ gradually intensified and, at the same time, the OH band of $SiO_2$ at 3744 $cm^{-1}$ attenuated. This is illustrated in Fig. 4A, where the values of integrated absorbance at 3660 and 3744 $cm^{-1}$ are plotted. A maximum for the band at 3660 $cm^{-1}$ and a minimum for that at 3744 $cm^{-1}$ appeared at 223 K.

When the sample was kept in $CH_2Cl_2$ vapor at high temperature (300–573 K) for 10 min and the spectra were then recorded in the presence of $CH_2Cl_2$ at 300 K, no spectral features different from those attributed to gaseous $CH_2Cl_2$ were observed. However, after degassing of the sample at 300 K, weak absorption bands remained at 2961, 2925, and 2852 $cm^{-1}$. Their intensities markedly decreased with the rise of the temperature and they were not detectable after treating the catalyst with $CH_2Cl_2$ at and above 473 K. No bands were seen in the frequency range 1300–1700 $cm^{-1}$.

Mass-spectrometric analysis of the gas phase showed that the decomposition of $CH_2Cl_2$ on Pd/$SiO_2$ proceeds above 350 K to produce HCl, $C_2H_4$, $CH_4$, and $H_2O$ (Fig. 3B).

Similar measurements were performed with the silica support alone. In the frequency range of OH groups we observed the same changes as described for Pd/$SiO_2$. In this case the changes in the OH frequency range occurred in a narrower temperature range. The highest absorption for the 3660 $cm^{-1}$ band and the lowest absorption for the 3744 $cm^{-1}$ band were obtained at 213 K (Fig. 4). Adsorption of $CH_2Cl_2$ on $SiO_2$ at 215 K produced much weaker absorption bands than the Pd/$SiO_2$. No detectable absorption bands remained in the spectrum after degassing at 233–243 K. In the products desorbing between 200 and 350 K we identified $CH_2Cl_2$ and small amounts of HCl and $C_2H_4$.

### 3.2. *Adsorption of $CH_2I_2$*

Some measurements also have been performed with $CH_2I_2$. Characteristic absorption bands for gaseous $CH_2I_2$ and $CH_2I_2$ adsorbed on Pd/$SiO_2$ are listed in Table 1.

When the sample was heated in the presence of $CH_2I_2$ from 213 K, a broad band centered at around 3630 $cm^{-1}$ was also observed, besides the band at 3744 $cm^{-1}$, characteristic for OH groups on the silica surface. The integrated absorption of this broad band showed a maximum at 266 K, and that of the 3744 $cm^{-1}$ band exhibited a minimum at the same temperature. This change is illustrated in Fig. 4. In the CH frequency ranges we observed spectral changes similar to those measured for $CH_2Cl_2$. The absorption bands, however, were very weak, and it was difficult to enhance them. The main reason is that this compound has a very low vapor pressure. Application of higher pressures of $CH_2I_2$ required the heating of the $CH_2I_2$ reservoir, which led to appearance of iodine in gas phase indicating the decomposition of the compound.

## 4. DISCUSSION

### 4.1. *Literature Survey of Surface Chemistry of $CH_2$-Containing Compounds*

Relatively little information can be found in the literature on the chemistry of adsorbed $CH_2X_2$ ($X$, halogens) (6–9). In the study of the interaction of $CH_2Cl_2$ with evaporated Pd films it was observed that the C–Cl bond is ruptured before any C–H bond breakage occurs. Mass-spectrometric analysis revealed the formation of $CH_4$ and $C_2H_4$ at 273–373 K. On Pd(100), under UHV conditions at 300 K, the complete dissociation of $CH_2Cl_2$ to C, Cl, and H occurred (9). The dissociation of $CH_2I_2$ was observed at

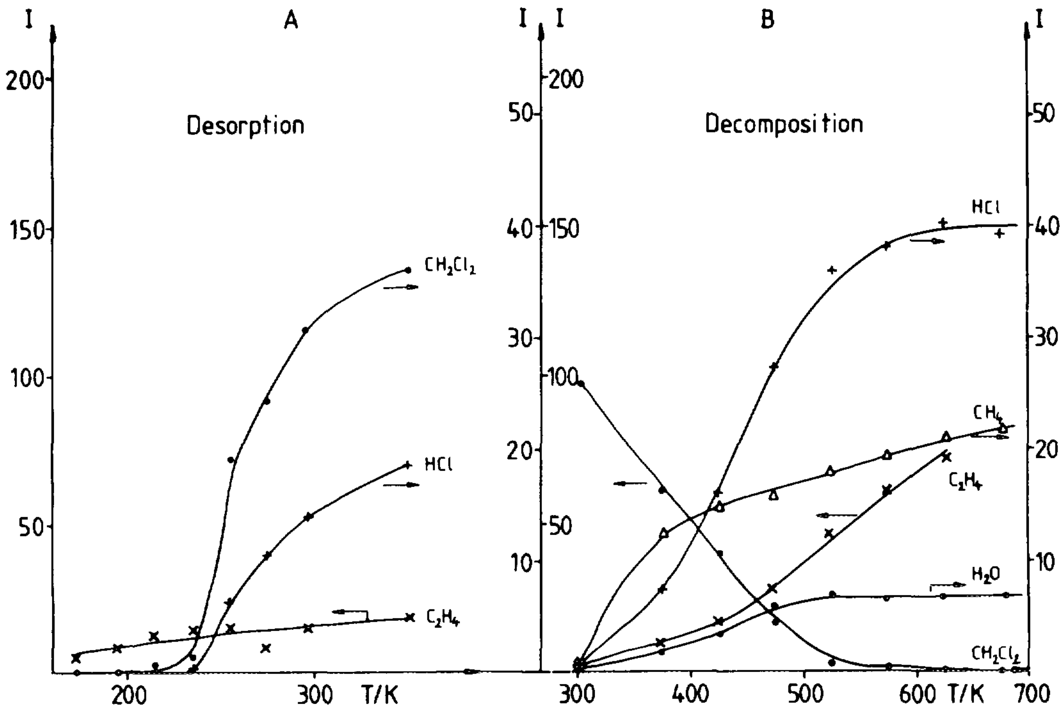


FIG. 3. Mass-spectrometric analysis of the gas phase during the heating of adsorbed CH$_2$Cl$_2$ (CH$_2$Cl$_2$ was adsorbed at 193 K and evacuated at the same temperature) (A) and during decomposition of CH$_2$Cl$_2$ (5 Torr) on Pd/SiO$_2$ at 300–700 K (B). The sample was kept at the selected temperature for 15 min before the temperature was raised.

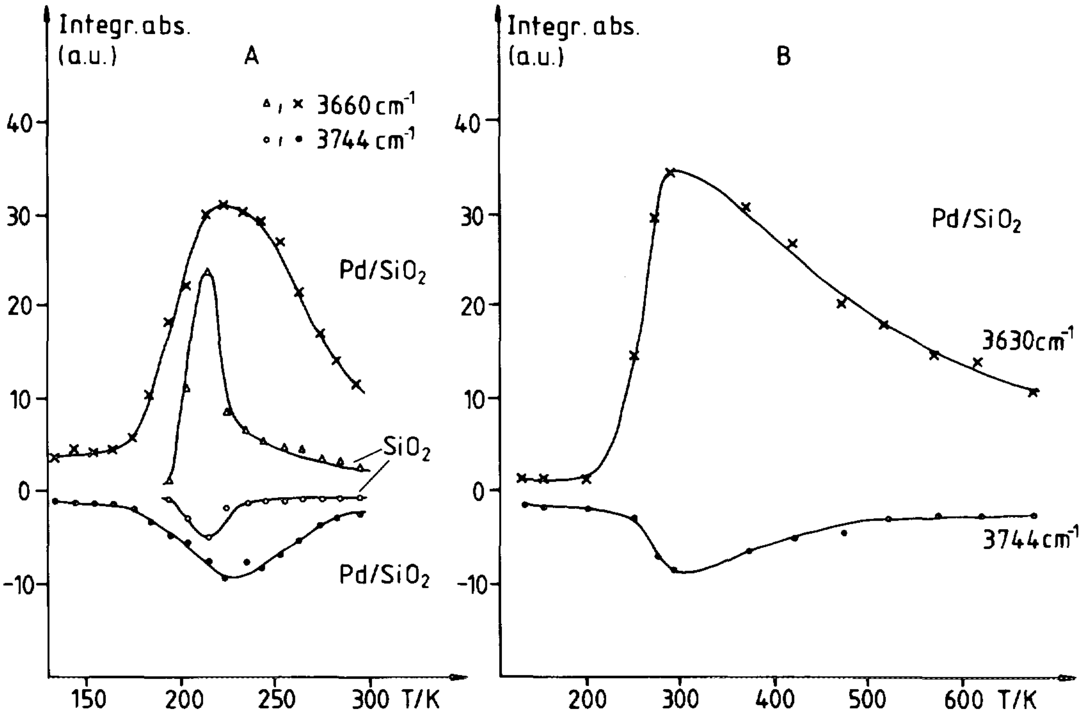


FIG. 4. Changes in the integrated absorbances of the bands observed in the OH region of IR spectra for Pd/SiO$_2$ and SiO$_2$ in the presence of CH$_2$Cl$_2$ (10 Torr) (A) and CH$_2$I$_2$ (1 Torr) (B) as a function of the adsorption temperature.

TABLE 1

Bands Characteristic for Gaseous and Adsorbed $CH_2Cl_2$ and $CH_2I_2$

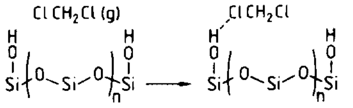
| Assignment | $CH_2Cl_{2(g)}$ (11, 12) | $CH_2Cl_{2(g)}$[a] | $CH_2Cl_2/Pd/SiO_2$ at 213 K[a] | $CH_2I_{2(g)}$ (13) | $CH_2I_{2(g)}$[a] | $CH_2I_2/Rh(111)$ (10) | $CH_2I_2/Pd/SiO_2$ at 213 K[a] |
|---|---|---|---|---|---|---|---|
| $\nu_{as}(CH_2)$ | 3045 (liquid) | | 3064 (liquid) | 3047 | 3047 | 3030 | 3057 |
| $\nu_s(CH_2)$ | 3007 (R) | 3004 | 2984 | 2970 | 2974 | 2940 | 2970 |
| | 2991 (P) | 2987 | | 2968 | | | |
| $\delta(CH_2)$ | 1473 (R) | 1473, 1464, 1457 | 1426 | 1343, 1353 | — | 1350 | — |
| | 1462 (P) | | | | | | |
| $CH_2$ wag | 1275.1 (R) | 1275 | — | | | | |
| | 1268.1 (Q) | | | | | | |
| | 1260.6 (P) | | | | | | |
| $\rho(CH_2)$ | 897.7 | 866 | — | — | — | 720 | — |
| | | | | 717 | | | |
| $\nu_{as}(C\text{-}X_2)$ | 763.5 (R) | — | — | 573, 571 | — | — | — |
| | 758.5 (Q) | — | — | | | | |
| $\nu_s(C\text{-}X_2)$ | 727.5 (R) | — | — | 487, 486 | — | | — |
| | 707.5 (P) | — | — | | | | |

[a] This work.

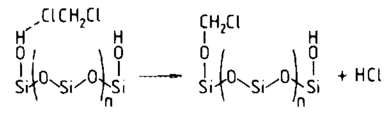
submonolayer coverage on Pd(100) at 90 K (2). The primary products of dissociation, $CH_2$ and I, were identified by photoelectron spectroscopy (XPS and UPS). A marked enhancement of the dissociation proceeded following illumination of adsorbed layer at 90 K (2). The $CH_2$ reacted to form methane and ethylene at 160–230 K. Similar features have been observed on Rh(111) surface, with the difference that the extent of coupling of $CH_2$ species was much less than on Pd(100) (10).

### 4.2. *Adsorption of* $CH_2Cl_2$ *on* $SiO_2$

The changes in the OH region of the $SiO_2$ spectra show the important role of surface OH groups in the adsorption processes of methylene halides. In response to the adsorption of these molecules the intensity of the sharp band at 3744 $cm^{-1}$ (due to free OH groups on the silica surface) is reduced, and a broad absorption appears on the low wavenumber side of this band indicating the presence of H-bridge-bonded surface species. It is noteworthy that after elimination of this broad absorption, the intensity of the 3744 $cm^{-1}$ band never reached its original value. All these phenomena indicate that: (i) Si-OH groups are involved in the development of H-bridge-bonded $CH_2X_2$ species and (ii) surface OH groups of silica are consumed in the formation of desorption products. We may consider that $CH_2X_2$ molecules interact with the protons of vicinal OH groups of silica with one of the halide ends.



On heating the adsorbed layer the broad absorption disappears as a result of the molecular desorption of $CH_2X_2$ molecules (detected by MS). In addition, however, the elimination of HCl also occurs, as indicated by the presence of HCl in the desorbing product.



If the $CH_2X_2$ interacts with both halide ends then the elimination of HCl (or HI) is accompanied by the formation of adsorbed $CH_2$ species, which decomposes or dimerizes into ethylene. The fact that $C_2H_4$ was also detected in the desorbing products may support this reaction scheme. It should be mentioned that the lowest integrated absorption value for the 3744 $cm^{-1}$ band and the highest absorption for the broad spectral feature were experienced at the same temperature. This temperature was 213 K for $CH_2Cl_2/SiO_2$ and 266 K for $CH_2I_2/SiO_2$ systems (Fig. 4).

Note that we observed the same features following the adsorption and desorption of $CH_3Cl$ on $SiO_2$ and $Pd/SiO_2$ surfaces (4). In that case the evolution of HCl and $CH_4$ was registered.

In the case of $CH_2Cl_2$ adsorption weak bands at 3064 and 2984 $cm^{-1}$ remained in the spectrum even after degassing the sample at 213 K. The 3064 $cm^{-1}$ band is close to the band attributed to liquid $CH_2Cl_2$ (Table 1). Therefore we assign these two bands to $\nu_{as}$ and $\nu_s$ of the liquid $CH_2Cl_2$.

### 4.3. *Adsorption of* $CH_2Cl_2$ *on* $Pd/SiO_2$

Following the adsorption and evacuation of $CH_2Cl_2$ at 213 K, we observed the same spectral features as for pure

TABLE 2

**High Resolution Electron Energy Loss Frequencies (in $cm^{-1}$) of Adsorbed $CH_2$ Species**

| Assignment | $CH_2$ (ex $CH_2CO$) on Ru(001) (*14*) | $CH_2$ (ex $CH_2N_2$) on Ru(001) (*15*) | $CH_2$ (ex $CH_2CO$) on Fe(110) (*16*) | $CH_2$ (ex $CH_2I_2$) on Rh(111) (*10*) |
|---|---|---|---|---|
| $\nu_a(CH_2)$ | 2945 | | | 2940 |
| $\nu_s(CH_2)$ | 2870 | 2965 | 2970 | — |
| $\delta(CH_2)$ | 1295 | | 1430 | — |
| $CH_2$ wag | 1065 | 1155 | 1020 | 1190 |
| $\tau(CH_2)$ | | | 930 | — |
| $\rho(CH_2)$ | 890 | 785 | 790 | 780 |
| $\nu_s(M—C)$ | | | 650 | 650 |

$SiO_2$. The difference is that the changes in the OH region occurred in a broader temperature range than $SiO_2$.

As regards the effects of Pd on the further reactions of $CH_2Cl_2$, we have to answer the following questions: (i) Are there any differences in the IR spectra of adsorbed $CH_2Cl_2$ on $SiO_2$ and $Pd/SiO_2$? (ii) Can we find any indication for the dissociation of $CH_2Cl_2$ over Pd and for the formation of $CH_2$ species? (iii) What are the stability and reaction products of $CH_2$ fragments on Pd?

To provide some general background, in Table 2 we have collected the vibrational characteristics of adsorbed $CH_2$ species produced on several metals by thermal dissociation of various $CH_2$-containing compounds. In Tables 3 and 4 data on the vibrations of adsorbed ethylene and ethylidyne ($CCH_3$), the possible products of $CH_2$ reactions, are presented for some relevant related systems.

From the comparison of the spectral data for the two samples, we can conclude that significant differences exist between $SiO_2$ and $Pd/SiO_2$. After the elimination of weakly adsorbed $CH_2Cl_2$ (disappearance of the band at 3064 $cm^{-1}$) from $Pd/SiO_2$ at 233–243 K, relatively intense bands remained in the spectra at 2985 and 2907 $cm^{-1}$, which are not detected, or hardly detected, on pure $SiO_2$. We may attribute these bands to chemisorbed $CH_2Cl_2$ on Pd, or to the $CH_{2(a)}$ species formed in the dissociation of $CH_2Cl_2$. Taking into account that the 2907 $cm^{-1}$ wavenumber is too low to be assigned to the symmetric stretch of $CH_2Cl_2$ (Table 1), the 2984 and 2907 $cm^{-1}$ bands are tentatively ascribed to the asymmetric and symmetric stretches of $CH_2$(a) species formed in the dissociation of $CH_2Cl_2$.

TABLE 3

**Vibrational Frequencies (in $cm^{-1}$) of Low-Temperature Adsorption Forms of Ethylene**

| Assignment | $Pt/SiO_2$ (21, 26) | $Pt/SiO_2$ (21, 26) | $Pt/Al_2O_3$ (23) | $Rh/Al_2O_3$ (23) | $Rh/SiO_2$ (24) |
|---|---|---|---|---|---|
| $\nu_{as}(CH_2)$ | — | — | — | 3080 | 3011 |
| $\nu_s(CH_2)$ | 3016 | 2922 | 2912 | 2966 | 2970 |
| $\nu(CC)/\delta(CH_2)$ | 1496 | [1428] | [1427] | 1509 | 1508 |
| $\delta(CH_2)/\nu(CC)$ | — | — | — | 1222 | — |
| Surface species | $\pi$ | di-$\sigma$ | di-$\sigma$ | $\pi$ | $\pi$ |

An alternative explanation is that the 2907 $cm^{-1}$ band is due to the vibration of ethylene formed in the dimerization of $CH_2$. However, we found no traces of a band at 1428–1509 $cm^{-1}$ (due to $\nu(CC)/\delta(CH_2)$) which would be decisive proof for the existence of ethylene on the surface.

Further spectral changes occurred above 263 K, when the 2907 $cm^{-1}$ band moved to 2922 $cm^{-1}$ and became more intense. At the same time a new band appeared at 2857 $cm^{-1}$. These spectral features correspond well to those of ethylidyne (Table 4). We tentatively assign these bands to the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ vibrations of ethylidyne surface complex. In this temperature range we observed the desorption of ethylene, but found no IR spectral indications for the presence of adsorbed ethylene. This suggests that adsorbed ethylene could not be accumulated to a detectable extent on $Pd/SiO_2$ during the decomposition of $CH_2Cl_2$, and/or its transformation into other surface complexes is fast. Note that in this temperature range adsorbed ethylene (the di-$\sigma$-bonded species) readily transforms into ethylidyne on metal surfaces (28–30).

On summing up the above considerations and taking into account the results obtained for Pd(100) surface (2), we can account with the following steps for the decomposition of $CH_2Cl_2$ on $Pd/SiO_2$ catalyst:

$$CH_2Cl_2 = CH_{2(a)} + 2\,Cl_{(a)}$$

$$CH_{2(a)} = C_{(a)} + 2\,H_{(a)}$$

$$CH_{2(a)} + 2\,H_{(a)} = CH_{4(g)}$$

$$Cl_{(a)} + \tfrac{1}{2}H_2 = HCl_{(g)}$$

$$2\,CH_{2(a)} = \pi\text{-}C_2H_{4(a)}$$

$$\pi\text{-}C_2H_{4(a)} = C_2H_{4(g)}$$

$$\pi\text{-}C_2H_{4(a)} = \text{di-}\sigma\text{-}C_2H_{4(a)}$$

$$\text{di-}\sigma\text{-}C_2H_{4(a)} = CCH_{3(a)} + H_{(a)}.$$

TABLE 4

Vibrational Frequencies (in $cm^{-1}$) Due to Ethylidyne ($-CCH_3$) Formed during $C_2H_4$ Adsorption

| Assignment | $Rh/SiO_2$ (24) | $Pt/TiO_2$ (25) | $Pt/SiO_2$ (21) | $Pt/SiO_2$ (26) | $(CH_3C)Co_3(CO)_9$ (27) | $Pd/Al_2O_3$ (23) |
|---|---|---|---|---|---|---|
| $\nu_{as}(CH_3)$ | 2936 | 2920 | — | — | 2950 | 2931 |
| $\nu_s(CH_3)$ | 2886 | — | 2880 | 2881 | 2890 | 2871 |
| $\delta_{as}(CH_3)$ | 1411 | — | — | — | 1420 | 1396 |
| $\delta_s(CH_3)$ | 1341 | 1335 | 1342 | 1342 | 1350 | 1331 |
| $\nu(CC)$ | — | 1115 | — | — | 1130 | — |

Note that the main product of the reactions of $CH_2$ species (produced by thermal- and photodissociation of $CH_2I_2$) on Pd(100) surface is ethylene (2). In the optimum case the ratio $C_2H_4/CH_4$ was 3.0–3.5. The high tendency of $CH_2$ for dimerization is in harmony with theoretical calculation, which showed that the activation energy of coupling of the species $CH_2$ on metal surfaces is only 6–9 kcal/mol (31).

In the brief study of the adsorption of $CH_2I_2$ on $Pd/SiO_2$ we observed spectral features that were in many respects similar to those measured for the adsorption of $CH_2Cl_2$. Small shifts in the characteristic absorption bands of gaseous $CH_2I_2$ to higher wavenumbers were experienced following its adsorption (Table 2). Changes in the intensities of the absorption in the OH region clearly demonstrate that the surface OH groups are involved in the bonding of $CH_2I_2$ on the surface, similarly as proposed for $CH_2Cl_2$ adsorption (subsection 4.1.).

Adsorbed $CH_2I_2$ is characterized by absorption bands at 3057 and 2970 $cm^{-1}$ in the high-frequency region. On the basis of the data collected in Table 1, these bands are assigned to the asymmetric and symmetric stretches of adsorbed $CH_2I_2$. Spectra of the annealed system qualitatively agreed with those observed for the $CH_2Cl_2$–$Pd/SiO_2$ system. Absorption bands were, however, very weak and prevented a more detailed analysis. Nevertheless, they indicate that the dissociation of $CH_2I_2$ also occurs on supported Pd to produce a $CH_2$ species, which probably undergoes similar reactions as observed following $CH_2I_2$ adsorption on Pd(100) surface (2) or following $CH_2Cl_2$ adsorption on $Pd/SiO_2$.

## 5. CONCLUSIONS

(i) Methylene chloride and iodide interact with OH groups of silica to form H-bridge-bonded species.

(ii) The dissociation of $CH_2Cl_2$ was observed on $Pd/SiO_2$ at 233–243 K, as indicated by the development of absorption bands at 2984 and 2907 $cm^{-1}$.

(iii) The $CH_2$ dimerized into $C_2H_4$ which partly desorbed and partly transformed into ethylidyne.

(iv) Ethylidyne is characterized by absorption bands at 2922 and 2857 $cm^{-1}$.

(v) $CH_2Cl_2$ decomposes on $Pd/SiO_2$ at a measurable rate above 350 K to give $C_2H_4$, $CH_4$, HCl, and $H_2O$.

(vi) $CH_2I_2$, due its lower vapor pressure, is a less suitable compound to produce $CH_2$ species on supported Pd.

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