Surface and Bulk Reactions of Carbon Tetrachloride with Titanium Dioxide

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Two different reactions occur between CCl_4 and TiO_2. At moderate temperature, the nature of the superficial reaction strongly depends on the hydration state of the solid. On a dry titanium dioxide, CCl_4 chemisorption on two bridges Ti–O–Ti gives a carbonyl complex detected by infrared spectroscopy. The reaction which follows from destruction of this complex proceeds by exchange of two superficial oxygen atoms for four chlorine atoms, with formation of gaseous CO_2. Strongly oxidizing Ti^{4+} ions, with high electron accepting properties, are created through the elimination of superficial oxygen atoms. On hydrated titanium dioxide, these reactions are followed by the formation of HCl which generates hydronium ions. Results obtained on TiO_2 and γ alumina point out the high reactivity towards CCl_4 of superficial oxygen atoms, compared to hydroxyl groups. Reticular reaction, which starts at 150°, is a proof of the relatively high mobility of the oxygen in the anatase lattice.

Introduction

The oxidation of hydrocarbons is generally catalyzed by transition metals or their oxides. The catalytic activity of these oxides is mainly determined by the bond energy, *i.e.*, the mobility of oxygen in the surface layer.[1] Until now, different types of superficial reactions have been studied to obtain information on the reactivity of superficial oxygen atoms: homomolecular exchange $^{16}O_2(g)$ $^{18}O_2(g)$[1–3] and $^{18}O_2(g)$ $C^{16}O_2(g)$,[4] heteromolecular exchange $^{18}O_2(g)$ $^{16}O(s)$, catalytic transfer of oxygen between CO and CO_2,[5] reduction of solids by CO[6] or H_2.[7]

From this standpoint, the study of carbon tetrachloride oxidation by mean of superficial oxygen atoms of a solid offers a double advantage. First this reaction characterizes the reactivity of superficial groups.[8] Second, exchange of oxygen atoms or hydroxyl groups by chlorine atoms may confer to the solid interesting catalytic properties.[9,10]

Gravimetric,[11] microcalorimetric,[8] and kinetic[12] studies have shown different types of interactions and reactions between CCl_4 and γ alumina. At room temperature, CCl_4 reaction with a fraction of the surface produces carbonate and CO_2. At 200°, reaction extends to the overall surface, its stoichiometry varies according to the hydroxyl group content. For a sample heated at 200°, CCl_4 exchanges one chlorine atom for one hydroxyl group; the obtained solid exhibits a weak Lewis acidity. For a sample heated above 300°, CCl_4 exchanges four chlorine atoms for two surface oxygen atoms; the study of redox character of such a solid by epr shows the existence of strongly oxidizing sites which have been identified as aluminum ions exposed through elimination of oxygen ions.[13] Above 230°, the attack of CCl_4 spreads into the lattice; the sublimation of $AlCl_3$ thus formed is detected above 300°.

In the present work, we have studied the oxidation of CCl_4 by TiO_2 in order to compare the oxidative character of TiO_2 with that of γ alumina. For this study we have mainly used infrared technique which is able to provide information on the reaction mechanism by identifying the intermediate superficial species.

Experimental Section

Materials. Titanium dioxide was supplied by the firm Degussa (Frankfurt am Main) as a crystalline and nonporous solid composed of anatase (85%) and rutile (15%). Before each experiment, samples are calcined under oxygen at 400° for 15 hr and desorbed under vacuum at 200° for 15 hr ($TiO_{2,(200)}$). The specific surface area of such material is 60 m^2/g, and about 50% of the surface is covered with hydroxyl groups (6 OH/100 Å^2). In some experiments, samples are calcined under oxygen at 400° for 15 hr and desorbed under vacuum at the same temperature for 15 hr ($TiO_{2,(400)}$); the solid obtained is completely dehydroxylated.

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(1) G. K. Boreskov, *Discuss. Faraday Soc.*, **41**, 263 (1966).

(2) A. P. Dzizyak, G. K. Boreskov, and L. A. Kasatkina, *Kinet. Katal.*, **3**, 81 (1962).

(3) G. K. Boreskov, A. P. Dzizyak, and L. A. Kasatkina, *ibid.*, **4**, 383 (1963).

(4) T. Kiyoura, *Bull. Chem. Soc. Jap.*, **39**, 2135 (1966).

(5) D. Y. Cha and G. Parravano, *J. Catal.*, **11**, 3, 228 (1968).

(6) P. Pichat and G. Brau, *J. Chim. Phys.*, **66**, 724 (1969).

(7) W. M. H. Sachtler and J. H. de Boer, *Proc. Intern. Congr. Catal., 3rd*, **1**, 252 (1964).

(8) J. Basset, M. V. Mathieu, and M. Prettre, *J. Chim. Phys.*, **66**, 1264 (1969).

(9) A. G. Goble and P. A. Lawrence, *Proc. Int. Congr. Catal., 3rd*, **1**, 320 (1964).

(10) J. Basset, F. Figueras, M. V. Mathieu, and M. Prettre, *J. Catal.*, **16**, 53 (1970).

(11) J. Basset, M. V. Mathieu, and M. Prettre, *Rev. Chim. Min.*, **5**, 879 (1968).

(12) J. Basset, M. V. Mathieu, and M. Prettre, *J. Chim. Phys.*, **66**, 611 (1969).

(13) J. Basset, C. Naccache, M. V. Mathieu, and M. Prettre, *ibid.*, **66**, 1522 (1969).

The γ alumina has been previously described;[11] before each experiment, this solid is calcined under vacuum at 500° for 15 hr; its specific surface area is 300 m^2/g and its hydroxyl content 2 OH/100 $Å^2$.

The different reactants are dried by treatment with P_2O_5 and molecular sieves 5A (Union Carbide) previously calcined; they are degassed by repeated freezing and evacuation before use.

Apparatus and Procedure. Infrared spectra are recorded with a Perkin-Elmer 125 spectrometer. Two types of cell have been used: a classical cell which allows the experiment to be done under controlled atmosphere at different temperatures, the spectra being recorded after cooling of the sample to room temperature,[14] and a high-temperature cell which allows the spectra to be recorded at the reaction temperature. Gravimetric, kinetic, and epr techniques have been described in previous papers.[11-13]

Results

A. Infrared Spectrometry. (1) Reaction of CCl_4 with Titanium Dioxide. The infrared spectrum of $TiO_{2,(200)}$ is characterized by ν(OH) bands at 3715, 3660, and 3410 cm^{-1}.[15] CCl_4 adsorption at room temperature modifies these bands and creates new species detectable by their bands in the region 4000–400 cm^{-1} (Figure 1).

The ν(OH) bands are replaced by a narrow one at 3540 cm^{-1} and by a very broad one centered around 3470 cm^{-1}. The position and the narrowness of the 3540-cm^{-1} band must be produced by a specific interaction between one hydroxyl group and one chlorine atom.

The presence of carbon dioxide is characterized by a weak band at 2350 cm^{-1} (ν_3). A band at 1700 cm^{-1} also appears; the same band is observed on alumina as well.

Gaseous or physisorbed CCl_4 is detected by its ν_3 vibration (790 cm^{-1}, 762 cm^{-1}) and by its combinations bands $\nu_1 + \nu_3$ (1250, 1230 cm^{-1}) and $2\nu_3$ (1550 cm^{-1}).

Heating the sample under CCl_4 at 100° does not produce marked modification of the spectrum except that the band at 1700 cm^{-1} disappears and the intensity of the CO_2 band at 2350 cm^{-1} increases. At 130°, the appearance of vibration rotation band of gaseous HCl, centered around 2890 cm^{-1}, is paralleled by the reduction of intensity of the ν(OH) bands at 3540 and 3470 cm^{-1}. Simultaneously a narrow band is formed at 1590 cm^{-1}. We shall see later that the same band is created by reaction of anhydrous hydrogen chloride with a $TiO_{2,(200)}$ surface. At 150°, the phenomena observed at 130° are more pronounced; consumption of hydroxyl groups, appearance of larger quantities of CO_2 and HCl and growth of the band at 1590 cm^{-1}. In addition two bands centered around 1400 and 1450 cm^{-1} are produced by the fixation of CO_2 on superficial oxygen atoms. At 200°, the elimination of hydroxyl groups is achieved. Simultaneously the intensity of HCl and CO_2 bands increases and the stretching bands ν_1 (1825 cm^{-1}) and ν_4 (849 cm^{-1})[16] of gaseous or physisorbed phosgene are observed. At this temperature there appears a band at 1700 cm^{-1}, attributed to chemisorbed phosgene. The intensity of ν_3 vibration of CO_2 increases, while the P and R combination bands of CO_2 appear at 3609 cm^{-1} ($2\nu_2 + \nu_3$) and 3716 cm^{-1} ($\nu_1 + \nu_3$) as well as the bands at 720, 665, 645, and 615 cm^{-1}. These bands are caused by transitions from excited states of ν_2 (667 cm^{-1}).[17] Finally, we observe at 490 cm^{-1}, a narrow band ($\Delta\nu_{1/2}$ = 10 cm^{-1}) which is attributed to ν_3 vibration of gaseous $TiCl_4$. At 300°, the intensity of the bands attributed to CO_2, HCl, and $TiCl_4$ considerably increases.

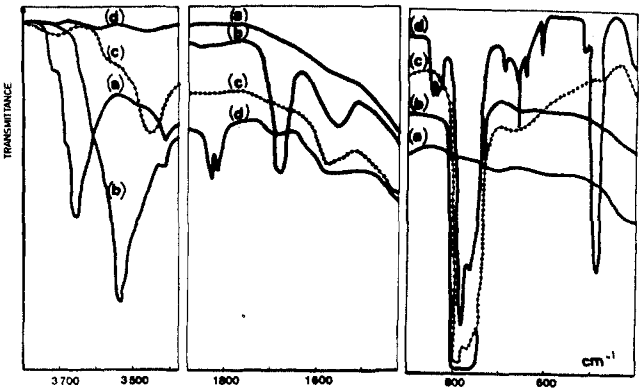

Figure 1. Infrared spectra of CCl_4 adsorbed in $TiO_{2,(200)}$: (a) initial solid, (b) after admission of 100 Torr of CCl_4 at room temperature, (c) after heating at 150° under CCl_4 for 8 hr, (d) after heating at 300° under CCl_4 for 10 hr.

After evacuation at room temperature, the spectrum of the solid is characterized by bands of low intensity associated with adsorbed CCl_4 and $TiCl_4$. The desorption of these compounds is performed at 100° under vacuum. In order to explain the origin of the different bands observed during the reaction of CCl_4 with TiO_2, we have studied the reaction of HCl and $COCl_2$ with TiO_2 and the reaction of CCl_4 with γ alumina.

(2) Reaction of HCl with Titanium Dioxide. The spectra resulting from the adsorption of HCl on TiO_2 at different temperatures are shown in Figure 2. At room temperature, the stretching bands ν(OH) of the initial solid are replaced by two maxima of absorption: the first at 3540 cm^{-1} is very sharp; the second centered around 3330 cm^{-1} is very broad. A narrow band at 1595 cm^{-1} is probably due to the bending vibration δ(OH) of molecular water which could be pro-

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(14) M. V. Mathieu and P. Pichat, "La Catalyse au Laboratoire et dans l'Industrie," Masson et Cie, Paris, 1967, p 319.

(15) M. Primet, P. Pichat, and M. V. Mathieu, *C. R. Acad. Sci.*, **267B**, 799 (1968).

(16) A. H. Nielsen, T. G. Burke, P. J. H. Woltz, and E. A. Jones, *J. Chem. Phys.*, **20**, 596 (1952).

(17) J. Lecomte, "Handbuch der Physik, Licht und Materie," Vol. XXVI, Part II, Springer-Verlag, Berlin, 1958, p 660.

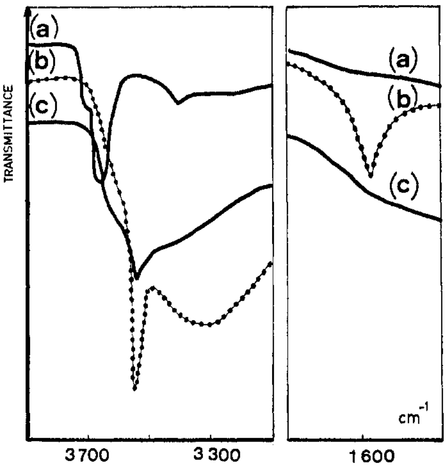


Figure 2. Infrared spectra of HCl adsorbed on $TiO_{2,(200)}$: (a) initial solid, (b) after admission of 100 Torr HCl at room temperature, (c) after heating at 300° under HCl for 9 hr and evacuation at 200° for 10 hr.

duced by the reaction of hydrogen chloride with superficial hydroxyl groups. Indeed, we have found the same band by chemisorption of water on TiO_2 chlorinated by CCl_4.

Heating at 300° under HCl, followed by cooling at room temperature, does not noticeably modify the intensity of these bands, but makes the band a 3330 cm^{-1} narrower and higher in frequency (3470 cm^{-1}). Evacuation at 25° decreases the intensity of δ(OH) and ν(OH) bands. At 200°, molecular water has disappeared and only a few OH groups remain on the solid.

(3) *Reaction of CCl_4 with γ Alumina.* The spectrum of γ alumina which is characterized by ν(OH) bands at 3795, 3735, and 3695 cm^{-1} is modified by the reaction of CCl_4 at room temperature, as was shown by Peri.[18] The (OH) bands are replaced by a very broad absorption maximum connected with the formation of hydrogen bands between the adsorbate and the hydroxyl groups. Besides, we observe bands in the spectral region 1800–1200 cm^{-1} (Figure 3): adsorbed CCl_4 is detected by its combination bands at 1550, 1250, and 1230 cm^{-1} and is completely desorbed by evacuation under vacuum at 200°; two bands at 1440 and 1360 cm^{-1} formed at room temperature are probably due to symmetric and antisymmetric stretching vibration of a monodentate carbonate. Heating at 200° makes them disappear and be replaced by a band at 1450 cm^{-1} caused by the antisymmetric stretching vibration of a carbonate ion; a broad band, centered around 1650 cm^{-1} is displaced higher in frequency on heating (1670 cm^{-1} at 70° and 1680 cm^{-1} at 160°) and disappears at 200°.

(4) *Reaction of $COCl_2$ with TiO_2 and γ Alumina.* Changes in the spectrum of a $TiO_{2,(400)}$, after adsorption of $COCl_2$ at room temperature, are shown in Figure 4. We find at 1825 cm^{-1} (ν_2) (high intensity) and

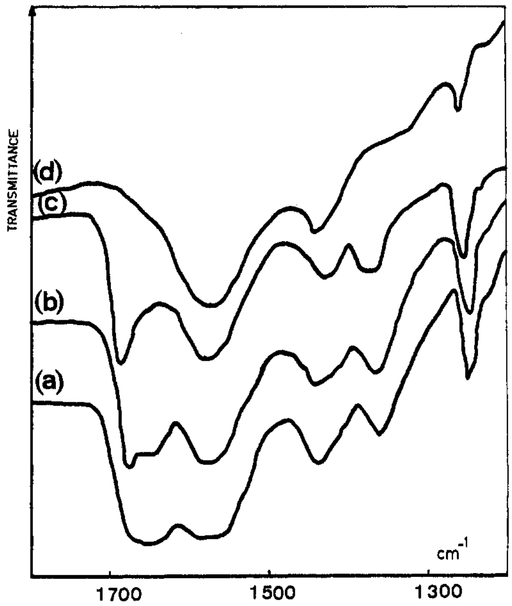


Figure 3. Infrared spectra of CCl_4 adsorbed on $Al_2O_{3,(500)}$: (a) initial solid after admission of 100 Torr CCl_4 at room temperature, (b) after heating at 70° under CCl_4 for 12 hr, (d) after heating at 200° under CCl_4 for 12 hr.

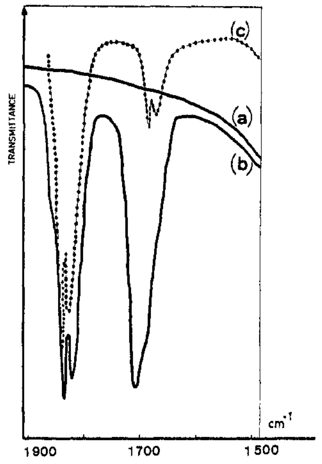


Figure 4. Infrared spectra of phosgene adsorbed on $TiO_{2,(200)}$: (a) initial solid, (b) after admission of 10 Torr of $COCl_2$ at room temperature, (c) gaseous phase.

1677 cm^{-1} ($2\nu_4$) (low intensity) the bands of gaseous $COCl_2$ and at 1820 cm^{-1} the fundamental band (ν_2) of physisorbed phosgene. We also observe an intense band at 1705 cm^{-1}. All of these bands are eliminated under vacuum at 25°.

γ alumina exhibits the same phenomena but the band situated at 1705 cm^{-1} associated with TiO_2 is displaced at 1690 cm^{-1} with γ alumina.

B. Gravimetric and Kinetic Results. Changes in weight registered during reaction of CCl_4 with $TiO_{2,(400)}$ at different temperatures are shown in Figure 5. Up to 130°, the initial increase in weight (part AB, curve 1)

[18] J. B. Peri and R. B. Hannan, *J. Phys. Chem.*, **64**, 1526 (1960).

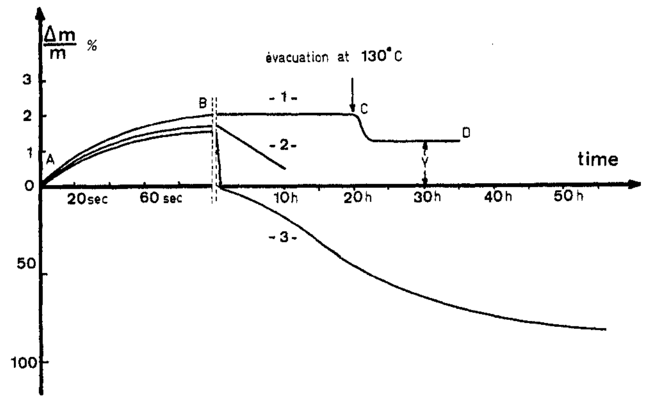


Figure 5. Changes in weight with time registered after CCl_4 admission on $TiO_{2,(400)}$ at various temperatures: (1) 130°, (2) 150°, (3) 200°.

is followed by a plateau (part BC, curve 1). This phenomenon must be connected with the CCl_4 adsorption and its reaction with the superficial oxygen atoms of the solid. The evacuation at this temperature (part CD, curve 1) removes the weakly adsorbed species (CCl_4 and CO_2). Stoichiometry of the superficial reaction has been defined by the ratio of the chlorine content to the increase in weight (Y) observed in D. The obtained value (1.41) is in agreement with the calculated one (1.30) for the exchange of one oxygen atom for two chlorine atoms.

Above 150°, the initial increase in weight is followed by a loss in weight (Figure 5, curve 2) which arises from the formation of gaseous $TiCl_4$. The attack of the lattice may be complete and the changes in weight with time obey a sigmoïd law, characteristic of gas–solid reactions with germination.[19] The activation energy, determined at the maximum rate between 200 and 270° has been found equal to 25 ± 2 kcal/mol.

Variations of chlorine content against reaction temperature are shown in Figure 6. In agreement with our infrared and gravimetric results, superficial reaction takes place at room temperature. Above approximately 150°, chlorine content is constant. Desorption between 200 and 400° of a $TiO_{2,(400)}$ chlorinated at 130° brings about a small change in chlorine content, which implies that the remaining chlorine is firmly bound.

The rate of chlorination has been measured by the quantity of CO_2 produced per second. At 200°, two successive phenomena have been observed (Figure 7). The rate first obeys a decreasing exponential law; the plateau coincides with the formation of gaseous $TiCl_4$.

Discussion

We can assume two different types of reaction between CCl_4 and TiO_2 to explain our gravimetric, kinetic, and infrared results. The first reaction, which takes place at a high rate, even at room temperature, is superficial. The second one, which is detected by the appearance of gaseous $TiCl_4$ at higher temperatures, concerns the attack of the lattice. We shall discuss these two kinds of reaction separately.

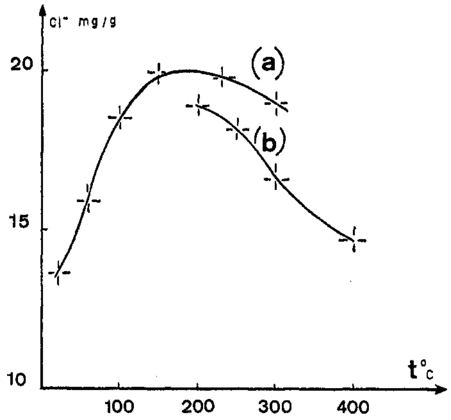


Figure 6. Thermal stability of superficial chlorine atoms: (a) effect of reaction temperature with $TiO_{2,(400)}$ on the chlorine content after evacuation at the reaction temperature, (b) effect of desorption temperature on the chlorine content for a sample of $TiO_{2,(400)}$ chlorinated at 130°.

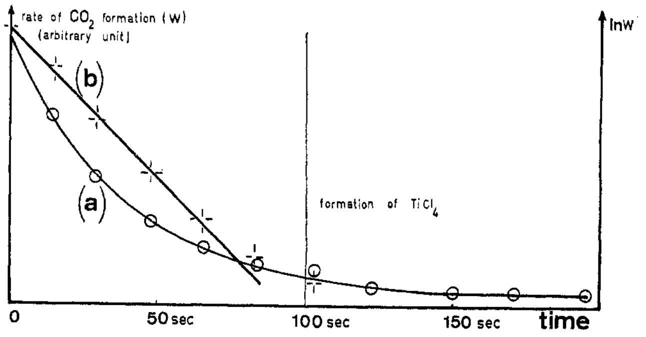


Figure 7. Kinetic data: (a) rate of CO_2 formation plotted *vs.* time during the reaction of CCl_4 with $TiO_{2,(400)}$ at 200°, (b) plots of $L_n(W)$ *vs.* time.

I. Reaction of CCl_4 with TiO_2 at Moderate Temperature

(*A*) *Nature of Superficial Reactions.* At room temperature, no hydrogen-containing product being detected, the CCl_4 reaction must occur with superficial oxygen atoms of TiO_2. The exchange of one oxygen atom for two chlorine atoms which, we have demonstrated on a dry $TiO_{2,(400)}$, takes place in accordance with the following equation

$$CCl_4(g) + 2O(s) \longrightarrow CO_2(g) + 4Cl(s) \qquad (1)$$

The mechanism of this reaction can be deduced from the infrared results obtained on alumina and titania. For these solids, CCl_4 chemisorption is connected with the formation of a band situated around 1700 cm^{-1} (1690 cm^{-1} for TiO_2 and 1680 cm^{-1} for γ alumina). Bands appear in the same region of the spectra

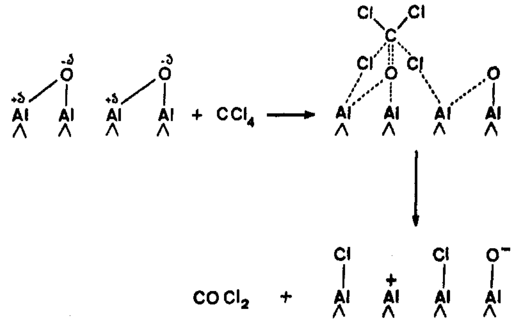
(19) B. Delmon, *Rev. Inst. Fr. Pétrole*, **13**, 472 (1963).

when phosgene is absorbed on titania (band at 1705 cm^{-1}) or γ alumina (band at 1690 cm^{-1}) at room temperature. These last bands cannot arise from the perturbation of the fundamental vibration ν(C=O) of phosgene, which is shifted to 1820 cm^{-1} by adsorption. Furthermore they cannot be due to the increase in frequency of the $2\nu_4$ vibration of phosgene which is less intense. These 1680–1705-cm^{-1} bands, although relatively low in frequency, can be assigned to carbonyl groups.[20] Scott[21] has shown that in carboxylates, the higher the frequency ν(C=O), the lower the electronic density on the oxygen, corresponding to the electronic release of alkyl radical. Likewise fundamental vibration ν(CO) of F_2CO is higher than that of Cl_2CO.[16] Therefore a low frequency for a vibration ν(C=O) is characteristic of an increase in electronic density on the oxygen.

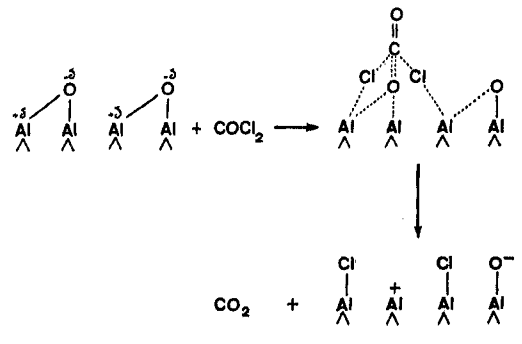
We have proposed below two models for the chemisorption and reaction of CCl_4 and $COCl_2$ on TiO_2 or Al_2O_3. These models account for the formation of electron-deficient titanium atoms, which attract electrons of the C=O band created by chemisorption. This explains the low frequencies observed for the ν(C=O) vibrations of chemisorbed phosgenes or CCl_4.

Schemes I and II. The complex I would account for the bands situated around 1700 cm^{-1} observed during the chemisorption of CCl_4 on alumina or titania; on titania it is formed at room temperature and destroyed at 70°, whereas on alumina its stability extends from 70 to 200°.

Scheme I



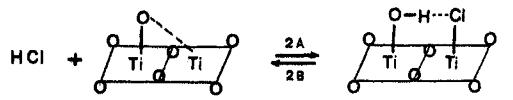
Scheme II



It is reasonable to suppose that, at room temperature, CCl_4 chemisorbs on Ti–O–Ti bridges and gives the complex I. The decomposition of this complex gives $COCl_2$. Since no band at 1820 cm^{-1} is detected at moderate temperature, chemisorption of phosgene according complex II must be followed by a rapid reaction which produces gaseous CO_2. The solid is then partially chlorinated and its chlorine content is about 4 Cl/100 Å^2.

The spectrum of adsorbed HCl, which exhibits a band at 3540 cm^{-1}, facilitates the assignment of the same band obtained by chlorination of TiO_2 with CCl_4 (3540 cm^{-1}, $\Delta\nu_{1/2}$ = 40 cm^{-1}). The most likely mechanism of HCl adsorption is a dissociative chemisorption[11,21] on Ti–O–Ti groups according to reaction scheme III.

Scheme III



(2)

Scheme III. Therefore, superficial chlorine atoms, created by reaction 1, cause the formation of hydrogen bonds with OH groups which are fixed to well-defined crystalline sites. The position and the narrowness of 3540-cm^{-1} band are then explained by the constant distance between chlorine atoms and OH groups as shown on the above scheme.

If temperature is raised to 130°, the rupture of these hydrogen bonds, according to reaction 2B, causes the appearance of gaseous hydrogen chlorine. In much the same way, the heating of a sample of HCl–chlorinated TiO_2 at 200° partially restores the Ti–O–Ti groups initially present on the solid.

The hydrogen chloride thus liberated can then react with OH groups, as was shown on alumina[11,22] or silica[23]

$$HCl(g) + Ti\text{-}OH \longrightarrow Ti\text{-}Cl + H_2O(ads) \qquad (3)$$

The Ti–O–Ti groups, created by the elimination of hydrogen chloride, can react again with CCl_4 according reaction 1. Simultaneity of reaction 1, 2B, and 3 explains most of the experimental results observed when the reaction temperature is raised: disappearance of hydroxyl groups; formation of hydrogen chloride and molecular water; increase of chlorine content with reaction temperature.

The band at 1590 cm^{-1} has been designated as a bending vibration, the nature of which has to be determined. It should be noted that the band is situated near the bending vibration of gaseous molecular water.[24] However its frequency is very low if we refer to gener-

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(20) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen and Co., 1968, p 154.

(21) J. Scott and R. Goulden, *Nature*, **220**, 5168, 698 (1968).

(22) J. B. Peri, *J. Phys. Chem.*, **70**, 1482 (1966).

(23) M. Baverez, B. Hatier, M. Bastick, and J. Bastick, *Bull. Soc. Chim. Fr.*, 1298 (1964).

(24) W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, **24**, 1139 (1956).

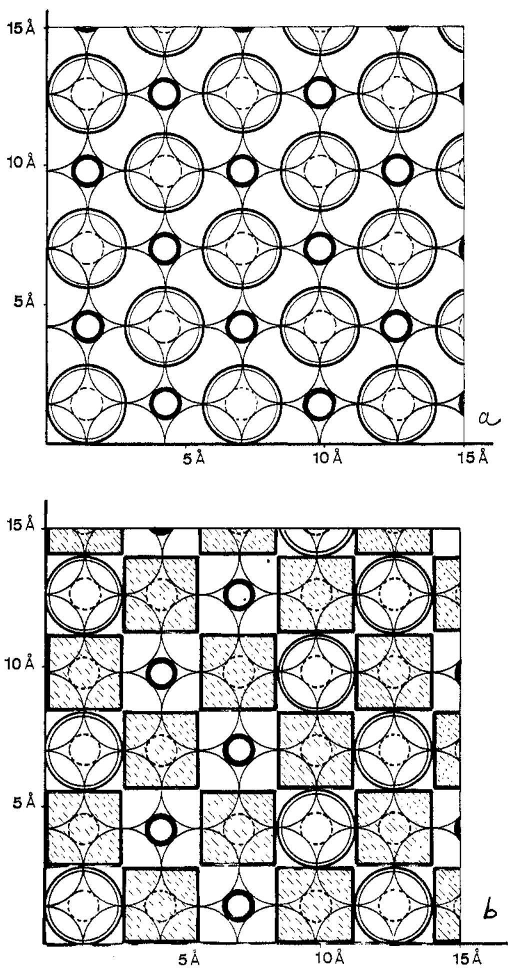

Figure 8. (a) Plane 001 of anatase surface wholly and regularly dehydroxylated: ◎, oxygen atom of the superficial layer; ○, oxygen atom of the lower layer; **○**, exposed titanium atom of the lower layer; ◌, titanium atom of the lower layer covered by a superficial oxygen atom. (b) transformation of model (a) after complete chlorination: ◎, unreacted oxygen atom of the superficial layer; ○, oxygen atom of the lower layer; ▨, chlorine atom; **○**, titanium atom exposed through the elimination of a superficial oxygen atom; ◌, titanium atom of the lower layer covered by a superficial oxygen atom.

ally known values, especially to results of Peri on chlorinated aluminas by HCl.[22] On these solids the hydrogen bands which are produced between molecular water and electronegative centers of the surface (chlorine or oxygen atoms) increase the force constant of the bending δ(OH). On the contrary, on our solids the highly oxidizing sites demonstrated by epr could adsorb water molecules forming coordinate bonds which utilize electron pairs of oxygen atoms.

The frequency δ(OH) of such a species could be as low as those already observed by Adams[25] and Baettie[26] in complexes of transition metals. But the adsorption of pyridine on TiO_2 chlorinated by CCl_4 is accompanied by the disappearance of the band at 1590 cm^{-1} and the formation of pyridinium ion which may be desorbed at 200°, whereas pyridinium ions detected on fluorinated aluminas persist until 500°.[27,28]

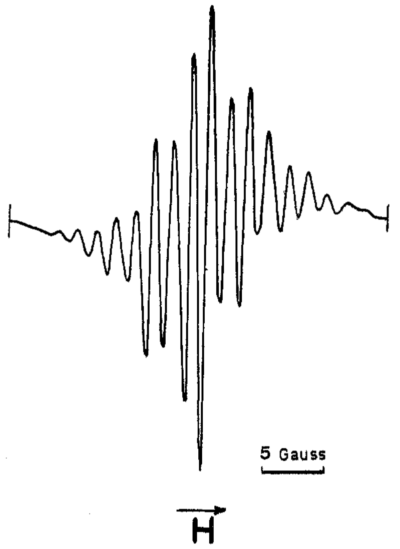

Figure 9. Epr spectrum of anthracene adsorbed on $TiO_{2,(400)}$ chlorinated by CCl_4 at 130° and desorbed at the same temperature.

It seems logical to attribute the disappearance of pyridinium ion to the sublimation of pyridinium chloride which could be produced from the species Cl^--H_3O^+ arising from the solvation of the proton of hydrogen chloride according to the reaction

$$H_2O(ads) + HCl(g) \rightleftharpoons [H_3O^+Cl^-](ads)$$

This hypothesis finds corroboration in the vibration frequency of hydronium ion in the compound H_3O^+-ClO_4^- [29] near 1590 cm^{-1}. On other chlorinated solids, a further study of formation conditions of the 1590-cm^{-1} band, and properties of the species responsible, should permit a distinction between the two hypotheses: chemisorption of water by coordinative ligand or formation of hydronium ions.

(*B*) *A Model for the Chlorinated Surface.* The surface of a wholly dehydroxylated titanium dioxide (face 001) holds six superficial oxygen atoms/100 Å². Complete exchange of these oxygens according to the proposed stoichiometry would give 12 Cl/100 Å². Whatever be the reaction temperature, maximum chlorine content is 6 Cl/100 Å², which proceeds from the exchange of half of the superficial oxygen atoms. Reaction of CCl_4 and $COCl_2$ in conformity with schemes I and II requires two Ti–O–Ti groups but only one oxygen is exchanged, so that the remaining oxygen cannot react.

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(25) D. M. Adams, private communication.

(26) I. R. Baettie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc., A*, **4**, 534 (1969).

(27) T. V. Antipina, O. V. Bulgarov, and A. V. Uvarov, *Proc. Int. Congr. Catal., 4th*, Moscow, Paper No. 79 (1968).

(28) T. R. Hugues, H. M. White, and R. J. White, *J. Catal.*, **13**, 58 (1969).

(29) R. C. Taylor and G. L. Vidale, *J. Amer. Chem. Soc.*, **78**, 5999 (1956).

We have represented in Figure 8a the 001 face[15,30] of a wholly and regularly dehydroxylated anatase. The same face, after complete chlorination is shown in Figure 8b. This model accounts for the exchange of 50% of superficial oxygen atoms by twice their quantity of chlorine atoms. Besides, this model shows electron-poor Ti^{4+} ions, the presence of which has been confirmed by epr study.

Anthracene is oxidized to its monopositive ion when chemisorbed on superficially chlorinated TiO_2. The high resolution of the hyperfine structure (Figure 9) can be connected with the existence of strongly oxidizing sites which possess a high-electron attractive power such as we have previously observed on chlorinated aluminas.[12] These sites could stabilize hydronium ions which have been detected on chlorinated TiO_2.

II. Reaction of CCl_4 with TiO_2 at 150° and Higher Temperatures

As was shown by gravimetric, kinetic, and infrared results, the first phenomenon observed above 150° when CCl_4 comes in contact with TiO_2 is a rapid superficial reaction. The attack of the lattice which proceeds afterwards is confirmed by three experimental facts: appearance of gaseous or physisorbed $TiCl_4$, loss in weight due to the sublimation of $TiCl_4$, and constant chlorine content of the solid above 150°.

This reticular reaction does not proceed according to the same mechanism as the superficial one. Besides, considering its high-activation energy (25 kcal/mol), it cannot progress at low temperature with a reasonable rate. The stoichiometry of this gas–solid reaction, which produces $COCl_2$, CO_2, and $TiCl_4$ would be

$$TiO_2 + 2CCl_4 \longrightarrow TiCl_4 + 2COCl_2$$

$$TiO_2 + CCl_4 \longrightarrow TiCl_4 + CO_2$$

Considering the oxidizing properties of titanium dioxide, it is not surprising that reticular reaction occurs on this solid at a lower temperature than on alumina. On alumina, $AlCl_3$ formation begins around 230°, and its sublimation begins at 300°.[11]

Conclusion

The mechanism of the surface chlorination of TiO_2 by CCl_4 has been specified by identification of carbonyl complexes detected by means infrared spectroscopy. Particular hydroxyl bands have been found which explain the formation of hydrogen chloride and the presence of hydronium ions. A model of the chlorinated surface has been proposed which accounts for the observed chlorine content and the presence of electron-deficient Ti^{4+} ions. Results obtained with TiO_2 and γ alumina point out the high reactivity towards CCl_4, of superficial oxygen atoms, compared to hydroxyl groups. Reticular reaction which begins at 150° indicates the relativity high mobility of oxygen in the anatase lattice.

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