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Study of the Interaction of Aliphatic Alcohols with TiO_2

III. Formation of Alkyl–Titanium Species during Methanol Decomposition

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The catalytic decomposition of methanol on both anatase and rutile forms of TiO_2 with a similar texture has been studied in connection with ir and TPD studies of the adsorbed phase. Coke poisoning readily occurs on rutile, even at 250°C, giving CH_4 as the main gaseous product. However, on anatase, bimolecular dehydration of methanol to ether can be followed in a narrow interval at 350–400°C, while coke poisoning occurred only at higher temperatures, leading to C_2H_6 in the gas phase. The formation of Ti–CH_3 species has been characterized by ir spectroscopy and by reaction with ethylene, which produces propylene through a Ziegler–Natta process. The same reaction leads to butenes during dehydration of ethanol through the formation of ethyl–titanium species. An interpretation of the differences in poisoning for the two oxides is given on the basis of the surface coordination of the more exposed Ti^{IV} ions.

INTRODUCTION

Parts I and II of this series (*1, 2*) were devoted to the study of the interaction of aliphatic alcohols from C_2 to C_5 with anatase TiO_2 surfaces. The conclusion was reached that alcohols are adsorbed in such a way as to complete the coordination of the Ti^{IV} ions on the surface, following the same pattern as observed by Bradley (*3*) for the respective titanium alcoholates (according to the donor and steric properties of the respective alcohols).

Decomposition of the adsorbed phase has been found to occur with all these alcohols through a monomolecular β-E_2 elimination mechanism leading to the corresponding olefin. While surface reaction was the slowest step of the catalytic cycle for all the alcohols, water was readily displaced from the surface by the alcohol vapors. However, in the case of EtOH, small amounts of ether and butenes were detected in addition to the main reaction, indicating the existence of bimolecular dehydration and oligomerization of the ethylene at the same time as the main monomolecular dehydration process.

Methanol, due to the lack of β-hydrogen in its molecule, does not allow a monomolecular dehydration process, and, for this reason, the study of its interaction and further decomposition on TiO_2 surfaces can give additional information on bimolecular dehydration to ether. Therefore the adsorption of this alcohol was studied to determine the mechanism of the bimolecular process. In order to ascertain the possible influence of the coordinative unsaturation of Ti^{IV} ions on the mechanism of this reaction, the study was extended, in this case, to both anatase and rutile forms of TiO_2. Previously reported models of both surfaces (*4, 5*) show different coordination spheres of the surface Ti^{IV} ions, thus allowing the analysis of this factor on the reaction.

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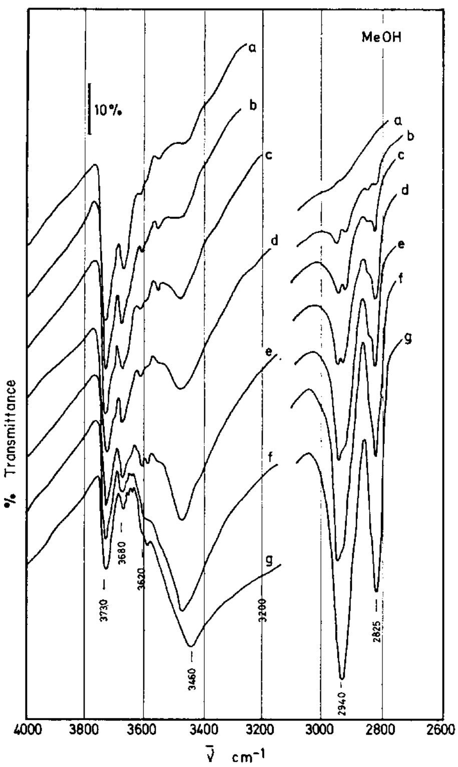


FIG. 1. Infrared spectra of methanol adsorbed on anatase (coverages in molecules nm^{-2}): (a) standard surface; (b) 0.41; (c) 0.82; (d) 1.36; (e) 1.84; (f) 2.30; (g) 2.58.

EXPERIMENTAL

Materials. The same anatase was used as in Parts I and II (*1*, *2*), while the rutile sample used for comparative purposes was, as in the case of the anatase, kindly supplied by British Tioxide (Code No. CL/D173/1), The rutile had been prepared in the same way as the anatase sample, by hydrolysis of titanyl sulfate, followed in this case by heating in air at 800°C. A study of the surface of this sample has been published elsewhere (*4*). Both the anatase and the rutile samples have the same pore size distribution of open V-shaped mesopores (*6*), so that differences in surface area (25.0 and 4.5 $m^2\ g^{-1}$, respectively) must be attributed to changes in the size of particles, as supported by electron microscope examination.

Methanol and ethanol from Merck (99% purity), redistilled on anhydrous $CuSO_4$, were subjected to several freeze–pump–thaw cycles before use. Titanium tetramethoxide was supplied by British Tioxide, while all other products used for gc identification were prepared by dehydration of the alcohols with H_2SO_4 or P_2O_5 and were purified by vacuum distillation followed by gc characterization.

Apparatus and procedures. Saturation coverages were determined volumetrically using 0.5–1.0 g of the sample in the same apparatus as used in Parts I and II (*1*, *2*). Temperature-programed decomposition (TPD) and ir experiments were performed as previously described, while catalytic activity was measured in a flow system, using a Pyrex glass reactor and furnace that allowed direct observation of the catalysts during the reaction. In addition, a small static reactor (67 ml in volume) was used in order to study the catalytic behavior of specially prepared samples. Gas-chromatographic analysis was performed in an F-7 Perkin–Elmer chromatograph provided with a flame detector using the same Par-I column as before (*1*, *2*).

The previously described "standard treatment" (*1*) was given to both anatase and rutile samples before all experiments. After this treatment, the surfaces were thoroughly characterized (*4*, *5*) by ir and TPD techniques which showed the surfaces to be almost fully dehydroxylated (2% of full coverage). Each run was carried out on a fresh sample unless otherwise stated.

RESULTS

Infrared Study of Adsorbed Methanol

Saturation of the surfaces of anatase and rutile with methanol gives an irreversible adsorption of ca. 2.3 MeOH nm^{-2}, whatever the structure of the sample. Figure 1 shows the ir spectrum of the anatase surface after adsorption of increasing doses of methanol. An interesting difference from other previously studied alcohols was observed. The ν_{CH} band of the alcohol at 2940 and 2825 cm^{-1} appears in this case split into two doublets at 2940, 2825 cm^{-1} and 2930, 2830 cm^{-1}. The bands at 2930, 2830 cm^{-1} were found in the ir spectrum of the titanium tetramethoxide /KBr and, therefore, were ascribed to alcoholate species. while the bands at 2940, 2825 cm^{-1} correspond to those of the alcohol, and their intensities readily increase with coverage. Plotting the ν_{OH} and ν_{CH} bands against the adsorbed amounts of alcohol, we observed patterns similar to those previously reported for ethanol (*1*). However, it is noteworthy that the bands at 3730 and 3680 cm^{-1}, due to residual hydroxyl groups on the anatase surface, remain almost unchanged up to a coverage of ca. 2 MeOH nm^{-2}; only the band at 3620 cm^{-1} increases in intensity, which suggests that the adsorption of methanol mainly involves O–H bond breaking to give MeO^- species. Coverages greater than 2 MeOH nm^{-2} lead to a "break point" in the intensities of the ir bands, similar to that previously observed for EtOH, suggesting a weak adsorption involving O^{2-} and OH^- species at the surface for higher coverages.

Displacement of water by methanol was studied in the same way as was done with ethanol, 2-propanol, and *t*-butanol (*1*). A standard anatase surface covered with ca. 1.8 H_2O nm^{-2} was exposed to an excess of methanol vapor and the effect of the adsorption of the alcohol was evaluated by a combination of ir and volumetric techniques. The behavior of methanol was similar to that previously reported for ethanol. After displacement, the total coverage was ca. 2 MeOH nm^{-2} plus 1 H_2O nm^{-2}. We noted a shift in the bending mode of the adsorbed water from 1600 to 1633 cm^{-1}, much higher than that observed in the case of ethanol (1618 cm^{-1}), which suggests a strong nucleophilic interaction of the methoxylate species which weakens the bond of coordinated water to the surface Ti^{IV} ions.

TPD Study of the Adsorbed Phase

The TPD trace characteristic of methanol adsorbed on anatase is shown in Fig. 2a. During TPD scanning, methanol was partially recovered unreacted, giving a broad peak centered at 200°C that corresponds to ca. 50% of the total coverage as in the case of ethanol (*1*) A second peak at higher temperatures, with a maximum at 335°C, was due to the bimolecular dehydration of the alcohol to dimethyl ether, the only possible dehydration process for this alcohol, while a third peak at 410°C was due to the formation of C_2H_6 contaminated with traces of CH_4. Gas-chromatographic analysis of the pulses using a Pye 104 chromatograph provided with a TC detector showed that, in addition to the above products, water was produced in the range 200–300°C during TPD scanning, while small amounts of CO, CO_2, and H_2 appeared at higher temperatures. Similar results were obtained with rutile, but, in this case, CH_4, CO_2, and CO were present in excess over C_2H_6 above 300°C during TPD, and the sample was dark brown at the end of the experiments.

Figure 2b shows the TPD traces of the sample covered with MeOH after an exchange experiment on a water-covered surface. The peak at 125°C was due to evolution of the water remaining at the surface (ca. 1 H_2O nm^{-2}). Gas-chromatographic analysis shows that formation of ether was lower than on the water-free surface. However, larger quantities of C_2H_6 were released at $t > 410$°C.

When the coverage of methanol on the standard anatase surface was lowered, the TPD traces shown in Fig. 3 were obtained, and gc analysis (not shown in the figure) indicates that for a coverage

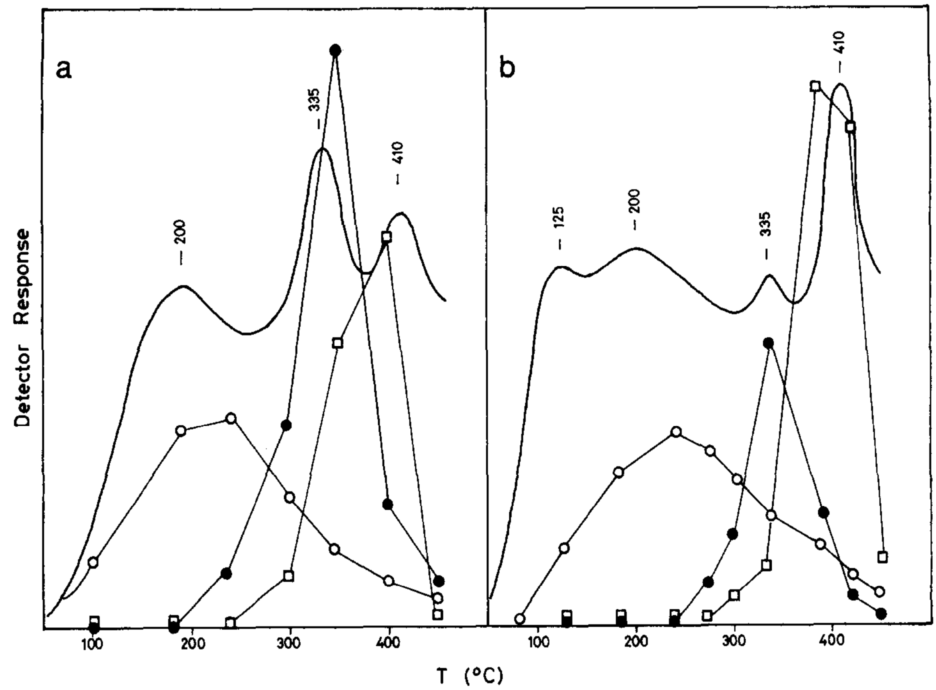


FIG. 2. TPD traces and gc analyses of pulses of methanol adsorbed: (a) on standard treated anatase (2.25 MeOH nm^{-2}); (b) after displacement of adsorbed water by methanol (2.05 MeOH nm^{-2} plus 0.75 H_2O nm^{-2}). (○) Methanol; (●) dimethyl ether; (□) ethane.

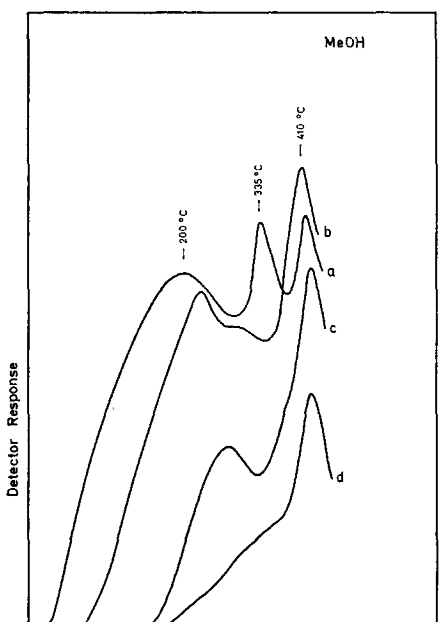


FIG. 3. TPD traces of methanol adsorbed on anatase at different coverages (in MeOH nm^{-2}): (a) 2.06; (b) 1.33; (c) 0.70; (d) 0.30.

of ca. 1 MeOH nm^{-2} only ether and ethane were evolved, while for coverages of ~0.3 MeOH nm^{-2} the TPD peak that remains at 410°C is produced almost exclusively by C_2H_6. Using different heating programs (β = 8, 16, 24, and 32°C min^{-1}) values of 104 and 163 kJ mol^{-1} were obtained for the activation energies of $(CH_3)_2O$ and C_2H_6 formation.

Thermal Evolution of the Adsorbed Phase

A detailed ir analysis showed that when an anatase surface covered until saturation with methanol was heated at 150°C, trapping the gas phase at 77 K, ca. 1 MeOH nm^{-2} of the alcohol remained on the surface, and the ir spectrum in the ν_{CH} region showed bands only at 2930 and 2830 cm^{-1}, characteristic of the CH_3 groups of the alkoxide. Analyses of the trapped vapors indicated the desorption of MeOH. The change in the ν_{CH} bands was followed after heating for several

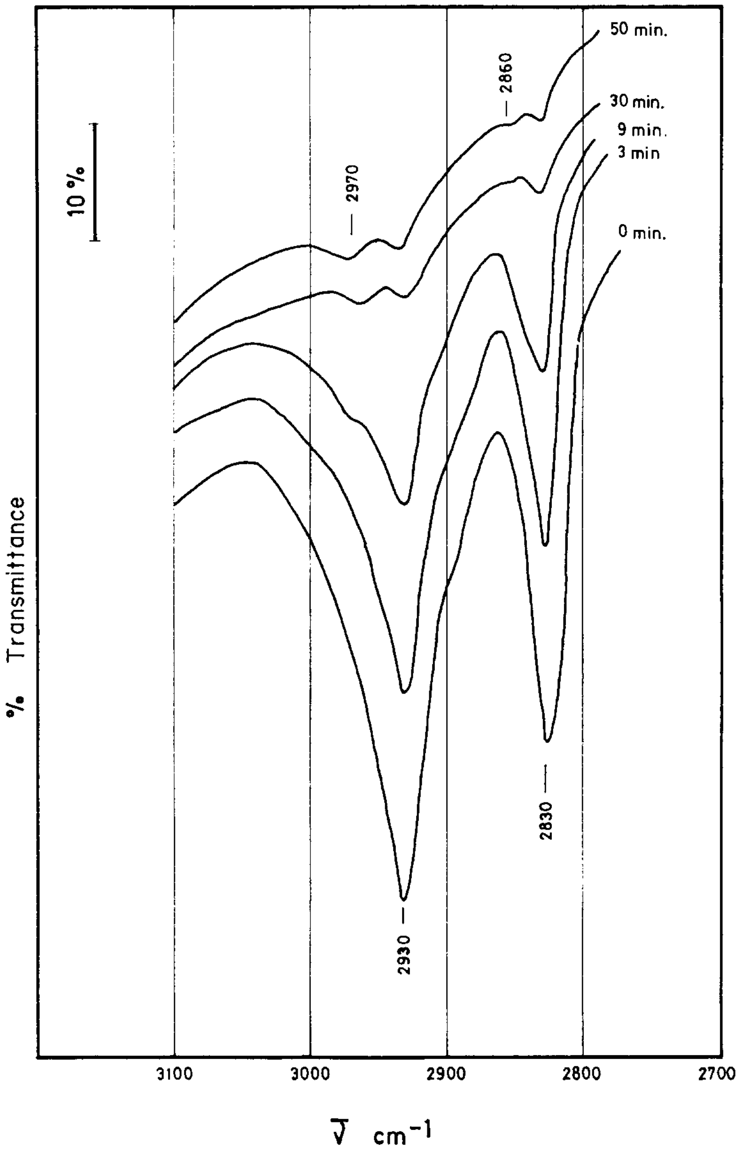


FIG. 4. Changes in the ν_{CH} bands of adsorbed alkoxide (CH_3O^- species) during heating under vacuum at 370°C.

periods of time while trapping the evolved gases at 77°K. At 310°C stabilization of the intensity of the ν_{CH} bands was obtained after heating for 45 min, but after 1 hr a small shoulder could be detected at 2970 cm^{-1}. At 370°C, the rate of evolution was faster, and, as shown in Fig. 4, the shoulder now appears after 10 min of heating. After 30 min at the same temperature, a splitting into two doublets at 2930, 2830 cm^{-1} and 2970, 2860 cm^{-1} could be clearly observed. At. 425°C, similar results were obtained, but removal of the bands was almost complete after 25 min, and only a small shoulder at 2970 cm^{-1} remained in this spectrum. Gas chromatographic analysis of the trapped gases during this set of experiments showed that only ether

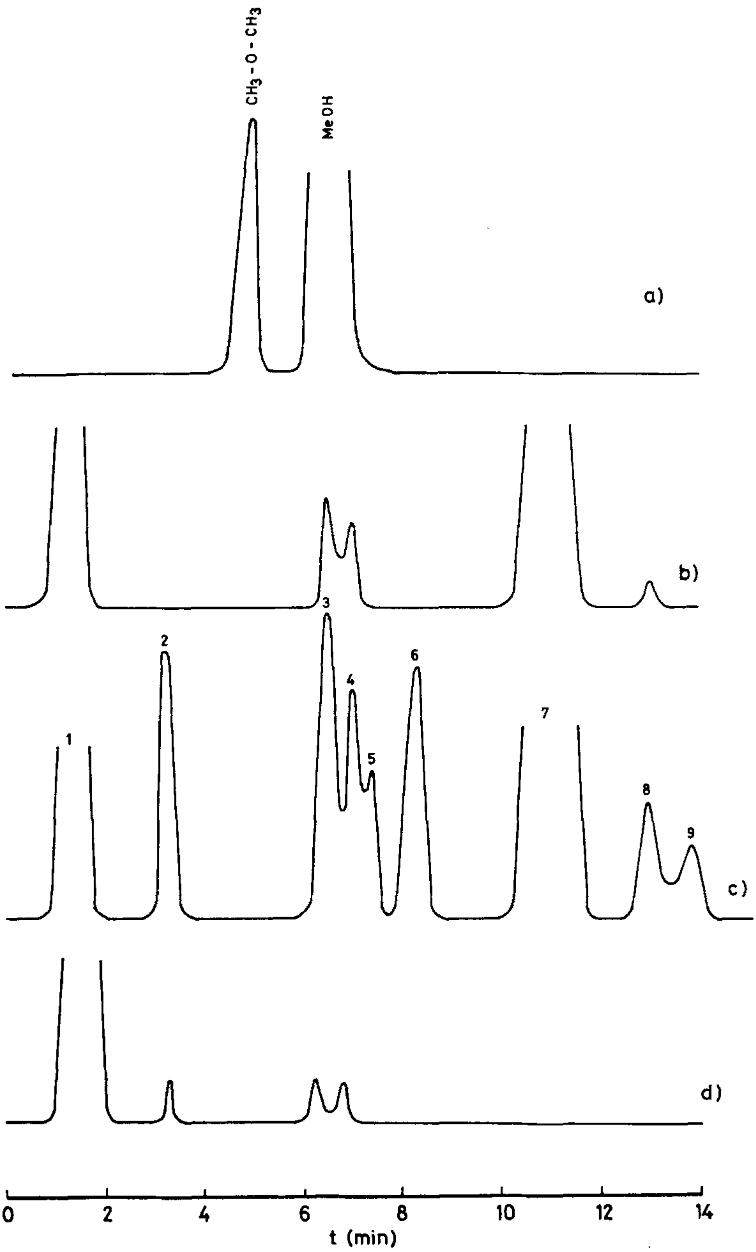


FIG. 5. Gas-chromatographic analyses of condensed species after reaction on anatase during 10 min at 280°C of: (a) 1.9×10^3 N m^{-2} of methanol; (b) 1.9×10^3 N m^{-2} of ethanol; (c) 1.9×10^3 N m^{-2} of ethanol on anatase with 0.29 MeOH nm^{-2} preadsorbed; (d) 1.9×10^3 N m^2 of ethylene on the same sample as c. *Species*: (1) ethylene; (2) propylene; (3) 1-butene; (4) *trans*-2-butene; (5) *cis*-2-butene; (6) methylethyl ether; (7) ethanol; (8) diethyl ether; (9) C_5 olefin.

and ethane were formed, the amount of the latter increasing as the temperature rose. The new doublet at 2970, 2860 cm^{-1}, which belongs neither to the adsorbed alcohol nor to the alcoholate species, was tentatively ascribed to Ti–CH_3 species formed on the surface at the higher temperatures on existing Ti^{III} ions, according to the reaction:

$$CH_3O^-_{ad} + Ti^{III} \longrightarrow Ti^{IV}\text{-}CH_3 + Ti^{IV}O^{2-} \quad (1)$$

Ziegler–Natta Oligomerization on Anatase

In order to check the above hypothesis relative to the Ti–CH_3 species, a set of experiments was performed using a static reactor. In these experiments 0.5 g of anatase either was used after the standard treatment or was covered with ca. 0.3 MeOH nm^{-2} (the amount giving the TPD peak of C_2H_6 at 410°C). The temperature was increased to 280°C before a known amount (1.9×10^3 N m^{-2} in a 67-ml volume) of methanol, ethanol, or ethylene was introduced into the reactor. After 10 min, the gas phase was trapped at 77 K and then was subjected to gc analysis. Figure 5 shows characteristic gc profiles from these experiments. When the reaction was carried out on a fresh sample with methanol, only dimethyl ether could be detected in the condensate together with the alcohol. Under the same conditions, ethanol yielded 1-butene and *trans*-2-butene in addition to ethylene, diethyl ether, and the alcohol itself. However, when a sample covered with 0.3 MeOH nm^{-2} was used for decomposition of ethanol at the same temperature, propylene, *cis*-2-butene, methylethylether, and a C_5 oligomer (according to Kovac indexing) were also formed. In this case, the amount of butenes was larger than in the previous experiment with ethanol on the standard anatase sample. After removal of the gas phase, a second run on the methanol-treated sample with a new dose of ethanol give smaller amounts of propylene and methylethylether, but larger amounts of butenes. Finally, when the reaction was carried out with ethylene on a sample with 0.3 MeOH nm^{-2}, only propylene, 1-butene, and *trans*-2-butene were detected. All these experiments suggest that, in addition to mono- and/or bimolecular dehydration of the alcohols, Ziegler–Natta oligomerization occurs on the anatase surface. Moreover, the presence of propylene from ethanol comfirms the formation of Ti–CH_3 species after pretreatment of the surface with 0.3 MeOH nm^{-2} at 280°C, probably according to the above reaction [Eq. (1)]. The number of Ti^{III} ions involved in such species, evaluated from the amount of MeOH which decomposed to C_2H_6 (Fig. 2), corresponds to ca. 10% of the exposed Ti^{IV} ions on the surface of anatase given our standard treatment (*5*).

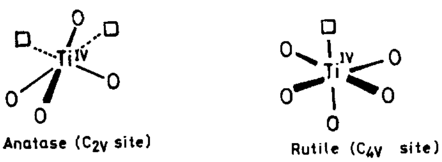
Catalytic Reaction

The catalytic activities of both rutile and anatase were studied in a flow reactor. Rutile samples readily darkened when methanol was allowed to flow at 350°C through the reactor and, in a few minutes, the catalyst became black due to the formation of coke on the surface, the decomposition reaction being completely poisoned, thus preventing any kinetic measurements. Gas-chromatographic analysis showed that, before poisoning, dimethyl ether, water, and methane were the main products of the reaction. With anatase, poisoning was much slower, and dimethyl ether could be obtained provided that the temperature remained within a narrow range (350–400°C), though slow poisoning prevented the evaluation of kinetic parameters. Poisoning readily occurred on anatase when the temperature was raised to 450°C, the main difference with rutile being the detection of C_2H_6 in excess over CH_4 in the decomposition products. The activity of the samples could not be restored by reconditioning in air, even at 500°C overnight. After this treatment the samples were gray-colored, and, when the experiment was repreated using them, they immediately became poisoned, thus again preventing any kind of kinetic study of the catalytic reaction.

DISCUSSION

According to the atomic models for rutile and anatase surfaces worked out on the basis of adsorption and spectroscopic data (*4*, *5*), exposed Ti^{IV} ions are in a fivefold (C_{4v}) coordination of O^{2-} on rutile, while, on anatase, they are in a fourfold (C_{2v}) coordination, which is supported by EPR studies of slightly reduced TiO_2 surfaces (*7*):

SCHEME I



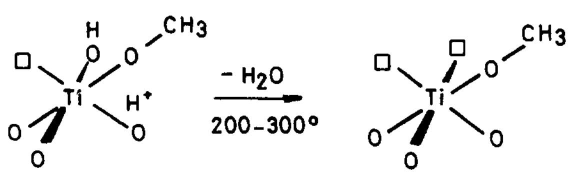
In fact, the actual surfaces of rutile and anatase outgassed at 350°C should hold different amounts of several types of OH groups in place of oxygen ions at the upper levels, while slight reduction produces low coordinated Ti^{III} ions which have been detected by EPR (*7*).

Adsorption of alcohols on almost dehydroxylated anatase surfaces occurs on the most exposed Ti^{IV} ions filling their coordination spheres, as previously stated (*1*). The ir study of methanol adsorption also supports this view. Thus, ca. 2 MeOH nm^{-2} becomes "tightly adsorbed" on anatase, in agreement with the calculated amount of Ti^{IV} ions in low coordination on this surface (1.9 Ti^{IV} nm^{-2}) (*5*).

In a first stage, up to 2 MeOH nm^{-2} coverage, methanol gives both alcoholate species from dissociative adsorption (raising the intensity of the 3620-cm^{-1} band) and coordinatively nondissociated adsorbed species, as shown by the splitting of the ν_{CH_3} bands in Fig. 1. After outgassing at 150°C the more labile molecular adsorbed species are removed, while 1 MeOH nm^{-2} remains adsorbed in the form of alcoholate species, a situation that we have reported in the case of other aliphatic alcohols (1, 2).

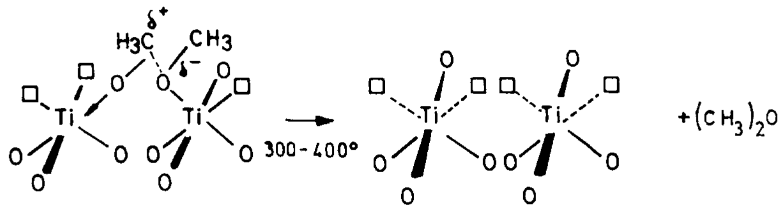
During TPD scanning of adsorbed methanol on anatase, dimethyl ether was formed in the range 300–400°C, while water desorbed from that oxide at 200–300°C (*1*); these facts suggest that, during TPD scanning of methanol, removal of OH^- and O^{2-} ligands from the coordination sphere of the cations occurs by reaction with H^+ from the dissociated species, leading to *coordinative unsaturation* on some of the Ti^{IV} cations. This process must be assisted by the strong *dislodging effect* of the nucleophilic MeO^- groups acting on the remaining ligands of the Ti^{IV} ions, as has been discussed elsewhere (*1*):

SCHEME II



As a result, very low coordinated Ti^{IV} ions must strongly withdraw electron density from the adsorbed alcoholate species. This fact enhances the electrophilic attack on its alkyl group by a nucleophilic oxygen from a "labile alcoholate" in a neighboring highly coordinated cation, thus leading to ether formation and restoring the original situation, except for the loss of surface hydroxyl groups:

SCHEME III



The existence of a high coverage of "labile alcoholate" species bonded to the originally fourfold-coordinated Ti^{IV} ions on the surface seems of paramount importance for ether production, as suggested by the differences in the height of the ether TPD peaks in Fig. 2 a and b. Moreover, if equilibrium is assumed, under catalytic conditions, between the species weakly adsorbed and the alcohol in the gas phase (through nondissociative adsorption), a kinetic equation involving a square root dependence on the alcohol pressure, similar to that observed by Knözinger *et al.* (*8*) for Al_2O_3, should be expected.

According to our previous interpretation with other aliphatic alcohols (*1*), the poisoning of the formation of ether by water observed in Fig. 2, together with the band at 1633 cm^{-1} for the bending mode of water remaining on the surface after the displacement experiment with methanol, suggests that some of this water blocks the coordination position in the neighborhood of the adsorbed alcoholate species, thus favoring the desorption of alcohol molecules in the initial stage of TPD scanning, probably reforming surface OH groups according to the reaction:

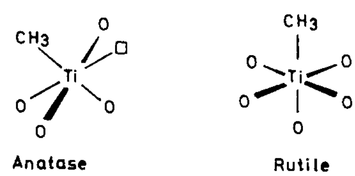
 (2)

instead of reacting with the tightly bonded MeO^- species to give ether.

In addition to the bimolecular process, reduction of Ti^{IV} ions to Ti^{III} or Ti^{II} seems to occur on the surface in the presence of alcohol vapor under mild thermal conditions, thus allowing some alkyl groups to react [according to reaction (*1*)] giving the alkyl species $Ti-CH_3$ characterized by ir frequencies at 2970 and 2860 cm^{-1}.

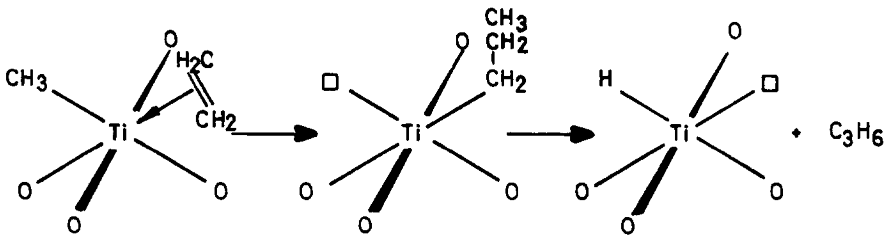
At the temperatures at which this process occurs (300–400°C), most of the electrons at the reduced surface must be in the 3d band, so that, according to the surface model of rutile, alkylation should, for the most part, produce completely sixfold-coordinated Ti^{IV} ions on the surface (i.e., they will change from five- to sixfold-coordination on alkylation); on anatase, however, coordinative unsaturation will remain (changing from four to five), even after alkylation, which may allow Ziegler–Natta polymerization. In fact, $Ti-CH_3$ species on the anatase surface have an environment rather similar to that found

SCHEME IV



on $TiCl_3$ solid polymerization catalysts (*9*), though, due to the higher electronegativity of the O^{2-} ligands, only oligomerization could be expected on TiO_2 according to the analysis of Henrici-Olivé and Olivé (*10*) of the influence of the remaining ligands on this process. Coordinative requirements for this reaction, therefore, are better fulfilled by anatase than by rutile surfaces, since the low coordinated Ti-CH_3 species on anatase allows ethylene insertion into a coordination vacancy. This insertion is followed by propylene evolution according to the well-known Cossee mechanism (*11*) for Ziegler–Natta polymerization:

SCHEME V



It is noteworthy that the role of the R_3Al cocatalyst in the classical Ziegler–Natta process was played here for the alcohol itself, acting first as reducing agent and then as alkyl reservoir.

Differences in coordinative unsaturation of the Ti–CH_3 species at the surfaces of rutile and anatase can also explain the different poisoning rates of the two forms of TiO_2 during catalytic decomposition of methanol. Dychokovskhy and Krusch (*12*) have shown, by labeling experiments, that decomposition of $Ti(CH_3)_4$ occurs through a mechanism involving carbene intermediates ($Ti{=}CH_2$) which finally leads to TiC and CH_4 according to:

$$Ti(CH_3)_4 \rightarrow TiC + 3\ CH_4. \qquad (3)$$

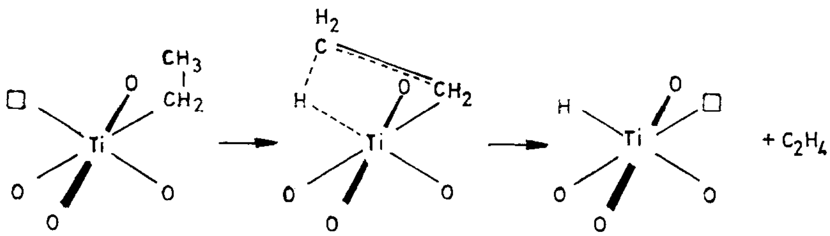
This mechanism seems to explain the decomposition reaction of the Ti–CH_3 species on the surface of rutile, as suggested by the formation of CH_4 and coke as main products during the first stages of catalytic decomposition of methanol and during TPD experiments. Most of the Ti–CH_3 species on rutile must be fully coordinated (sixfold), which, according to Cotton and Wilkinson (*13*), increases their thermal stability by disallowing easy pathways for decomposition. On the other hand, in the case of anatase, the unsaturated coordination of the Ti–CH_3 sites (four or five) may allow the formation of dialkyl species ($>Ti(CH_3)_2$) which decompose through a reductive elimination pathway, giving C_2H_6 with an activation energy of 163 kJ mol^{-1}:

$$Ti^{IV}(CH_3)_2 \rightarrow Ti^{II} + C_2H_6. \qquad (4)$$

This concerted mechanism is now well established in the chemistry of the metallocenes (*14*) and can occur on anatase due to the possibility of bringing together two CH_3 ligands at the same metal center, a situation which is less likely on the rutile surface. However, when anatase is heated during the catalytic process at temperatures greater than 450°C, reduction of the surface will increase and new Ti–CH_3 species should be formed by realkylation. Competitive carbene decomposition leading to coke formation and poisoning would now be favored because of an entropy effect at these higher temperatures; thus, the poisoning of anatase under these conditions can be explained.

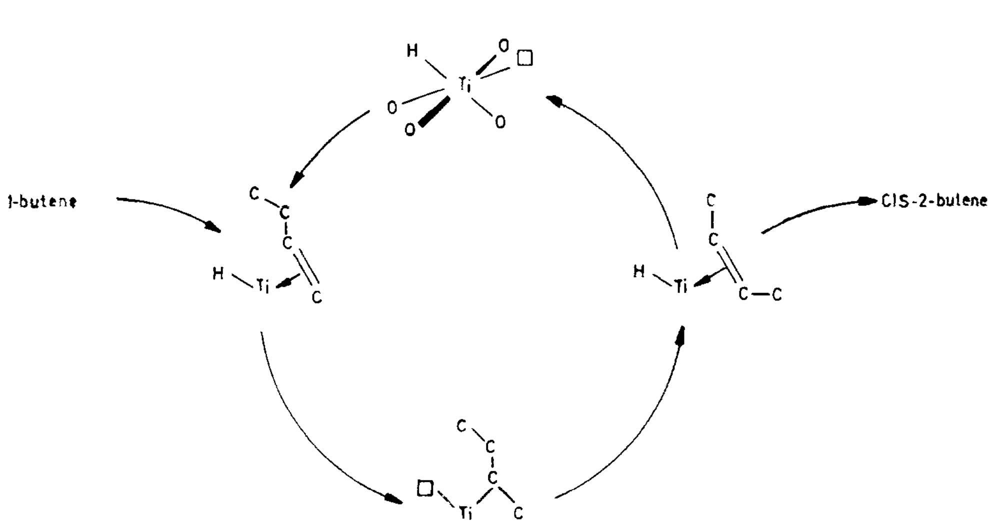
Previously reported formation of butenes during dehydration of ethanol on anatase (*1*) is now easily understood by assuming that Ti–C_2H_5 species are also formed from adsorbed ethanol. However, in this case, alkyl elimination partially occurs via a hydrogen β-elimination according to:

SCHEME VI



leaving Ti(H)(□) sites on the surface. The lack of oligomerization products when using aliphatic alcohols higher than ethanol (*2*) suggests that such a β-hydrogen elimination from the corresponding Ti–alkyl species readily occurs. On the other hand, insertion of the bulky and less basic olefins must be rather unfavorable, thus preventing the oligomerization process during decomposition of these higher alcohols. However, the existence of these Ti–C_2H_5 species, even though kinetically labile (because of the β-elimination pathway), directly accounts for 1-butene formation during dehydration of ethanol, which can be followed by isomerization through a Markownikow addition–elimination mechanism on the same Ti(H)(□) centers:

SCHEME VII



giving *cis*-2-butene. This preference over an anti-Markownikow addition has been shown previously by Lake and Kemball (*15*) in the case of propylene to explain their isotopic exchange results on rutile.

Isomerization of butenes on rutile surfaces, where the number of $\mathrm{Ti}{<}^{H}_{\square}$ centers should be lower than on anatase, has been studied by Shannon *et al.* (*16*), who observed that at $t > 200°C$, all six possible interconnecting reactions take place, though the only kinetically favored processes were the formation of *cis*-2-butene from 1-butene and the double-bond migration with *cis*-2-butene. We reported (*2*) rather similar behavior during dehydration of butanols on the same anatase sample, in which two types of centers, one for 1-butene/*cis*-2-butene and another for *trans*-2-butene formation, were assumed. The site symmetry of the Ti^{IV} centers is not only important for 2-butanol dehydration leading to 1-butene/*cis*-2-butene or *trans*-2-butene, but also for isomerization of 1-butene into *cis*-2-butene; the same type of centers are probably active in both reactions, though the oxidation state of the titanium ions could be different. Indeed, the data in Fig. 5, showing that *cis*-2-butene appears only when an excess of 1-butene in the gas phase competes with ethylene, indicate that the centers for 1-butene and *trans*-2-butene formation from ethylene are different.

Insertion of the olefin into the $\mathrm{Ti}{<}^{H}_{\square}$ sites supports the conclusions of Shannon *et al.* (*16*) that double-bond migration has a rate determining step involving C–H bond breaking. The observation that heavy water (but not D_2) strongly poisons isomerization but leads to deuterium in the products could be explained if heavy water reacts with Ti^{III} ions, produced by *in situ* reduction of the surface by the butenes at $t > 200°C$, according to:

$$D_2O + 2\,Ti^{III} \longrightarrow Ti^{IV}\text{-}OD + Ti^{IV}{<}^{D}_{\square} \qquad (5)$$

Therefore, each *cis*-2-butene molecule formed by isomerization of 1-butene can acquire a deuterium atom, as reported by Shannon *et al.* (*16*).

The evidence given in this paper on the formation of Ti–alkyl species on the surface of TiO_2 does not allow ruling out this mechanism, as suggested by Shannon *et al.* (*16*) but, on the contrary, makes it very likely.

In summary, we may conclude that Ti–alkyl species are important intermediates for the side reactions taking place on the surface of TiO_2 during decomposition of aliphatic alcohols. Oligomerization, isomerization, and reductive elimination reactions occur on both anatase and rutile surfaces during dehydration of these alcohols. On rutile, but not on anatase, the higher coordinative saturation of the Ti^{IV} ions at the surface leads to rapid poisoning of the catalyst, giving a clear example of the importance of coordination state of the surface cations on the catalytic properties of oxides.

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