Infrared Investigation of the Adsorption and Reactions of Methanol on V$_2$O$_5$/TiO$_2$ Catalysts[†]

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The oxidation of methanol on a V$_2$O$_5$/TiO$_2$ monolayer catalyst was studied by infrared spectroscopy using transmittance and diffuse-reflectance cells. Methanol was adsorbed on the catalyst surface at room temperature to form methoxy groups. Upon heating to 150 °C, these groups were oxidized to oxymethylene species. The latter species were also formed by adsorption of formaldehyde. When nitrogen saturated with methanol vapor was passed over the catalyst continuously at 150 °C, methoxy, oxymethylene, and formate groups were formed successively. Formaldehyde, methyl formate, dimethoxymethane, and CO were detected simultaneously in the gas phase. When the gas stream was stopped, the formation of these products did not stop immediately; this indicates that the observed surface species are reaction intermediates. On the basis of these results, a mechanism is proposed for the reaction. The results are also compared with those obtained with TiO$_2$ alone; it is concluded that the different oxidation behavior of the support alone is due to different strengths of the C–H bond of the methoxy groups when adsorbed on the support and on the V$_2$O$_5$/TiO$_2$ surface.

Introduction

V$_2$O$_5$ is a well-established catalyst for selective oxidation reactions. The bulk oxides cannot generally be used in industrial processes because of their lack of thermal and/or mechanical strength. However, when the active phase is applied on a support, the stability of the catalyst can be greatly increased. In previous work,[1–3] it was shown that the catalytic properties of the vanadia phase can be greatly influenced by the nature of the support. It is obvious that the effect of the support will be greatest when the active phase is present as a monomolecular layer. We also showed that when methanol was adsorbed on a metal oxide, heating and oxidation lead to various end products, such as formaldehyde, methyl formate, dimethoxymethane, dimethyl ether, carbon monoxide, carbon dioxide, hydrogen, and water, depending on the nature of the catalyst.[3]

Several different mechanisms have been proposed for the oxidation of methanol, these being based on infrared spectroscopy studies of intermediate species.[4–7] For example, Busca and Lorenzelli[4] suggested that methanol adsorbed on α-Fe$_2$O$_3$ reacts first with hydroxyl groups to form methoxy groups and that these later form formate groups. Groff and Manogue[5] found the same surface species on TiO$_2$ at 400 °C. The formate groups were formed by the readsorption of formaldehyde formed in an earlier reaction step. Decomposition of these formate groups was thought then to give H$_2$ and CO$_2$ by dehydrogenation or H$_2$O and CO by dehydration. Hey and Ekerdt also found these groups after adsorption of methanol on ZrO$_2$;[6] they suggested that oxymethylene was formed as an important intermediate. Bazilio et al.[7] sug-

gested that the same intermediate could explain the oxidation of methanol on silver.

Previous papers from our group[1–3,8] have described the preparation of monolayer catalysts of vanadium oxide on TiO$_2$; these materials were shown to be good catalysts for the selective oxidation of methanol to formaldehyde. In this study, we attempt to elucidate the mechanism of the methanol oxidation on these V$_2$O$_5$/TiO$_2$ monolayer catalysts by measuring the infrared spectra of the species resulting from the adsorption of methanol in static adsorption experiments as well as under the methanol oxidation conditions. Using the differences in the infrared spectra, we give an explanation of the differences in selectively for formaldehyde formation between the methanol oxidation reaction over V$_2$O$_5$/TiO$_2$ and that over TiO$_2$ alone.

Experimental Section

The V$_2$O$_5$/TiO$_2$ monolayer catalyst was prepared by bringing a toluene solution of vanadyl acetylacetonate into contact with TiO$_2$ for 3 h at a temperature of 102 °C. The TiO$_2$ was obtained from Degussa; it contained 32% rutile and 68% anatase. The BET surface area is 50 m^2/g, and this remains constant when the vanadium oxide has been brought onto the surface. The vanadium content of the catalyst studied was 1.7%, indicating that the vanadium oxide layer does not completely cover the surface.[1] When cell I or II was used (see below), either 0.3 or 0.02 g of the catalyst was pressed into a disk (thickness 0.1 mm) and placed in the infrared cell. In order to remove adsorbed water before starting an experiment, the catalyst was heated at about 400 °C for half an hour in air and another half an hour in vacuum or nitrogen atmosphere.

The infrared spectra were taken with a Nicolette FTIR M-XS spectrometer, using three different cells:

(i) For the adsorption-type experiments, cell I was used; this allows both analysis of the adsorbed species and of the gas phase in equilibrium with the catalyst in a constant closed volume. The V$_2$O$_5$/TiO$_2$ catalyst was first exposed to methanol or formaldehyde at room temperature. The cell was then slowly heated and spectra of both the catalyst and the gas phase were taken from time to time.

(ii) For experiments under dynamic conditions, a special cell, cell II, was designed; this has a short path length through the gas phase and is attached to a flow system used for measuring flows of nitrogen gas. The N$_2$ flow rate used for the measurements was 0.8 cm^3 s^{-1}. The nitrogen gas, in which traces of oxygen were

[†] Presented at the "Kiselev Memorial Symposium", 60th Colloid and Surface Science Symposium, Atlanta, GA, June 15–18, 1986; K. S. W. Sing and R. A. Pierotti, Chairmen.

(1) Van Ommen, J. G.; Hoving, K.; Bosch, H.; Van Hengstum, A. J.; Gellings, P. J. *Z. Phys. Chem.* **1983**, *134*, 99. Van Hengstum, A. J.; Van Ommen, J. G.; Bosch, H.; Gellings, P. J. *Appl. Catal.* **1983**, *5*, 207. Van Hengstum, A. J.; Van Ommen, J. G.; Bosch, H.; Gellings, P. J. In *Proceedings of the 8th International Congress on Catalysis, Berlin*; Verlag Chemie: Weinheim, 1984; Vol. 4, p 297.

(2) Bond, G. C.; Koenig, P. *J. Catal.* **1982**, *77*, 309. Bond, G. C.; Brueckman, K. *Faraday Discuss. Chem. Soc.* **1981**, *72*, 235.

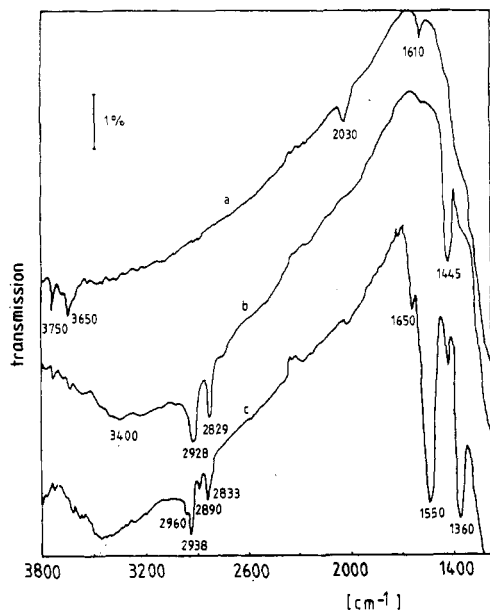(3) Gasior, M.; Gasior, I.; Grzybowska, B. *Appl. Catal.* **1984**, *10*, 87.

(4) Busca, G.; Lorenzelli, V. *J. Catal.* **1980**, *66*, 155.

(5) Groff, R. P.; Manogue, W. H. *J. Catal.* **1984**, *87*, 461.

(6) He, M. Y.; Ekerdt, J. G. *J. Catal.* **1984**, *87*, 381.

(7) Bazilio, C. A.; Thomas, W. J.; Ullah, U.; Hayes, K. E. *Proc. R. Soc. London, A* **1985**, *399*, 181.

(8) Van Hengstum, A. J.; Van Ommen, J. G.; Bosch, H.; Gellings, P. J. *Appl. Catal.* **1983**, *8*, 369.

Figure 1. Infrared spectra of V_2O_5/TiO_2 recorded (a) before adsorption of methanol at room temperature, (b) after adsorption and evacuation at room temperature, and (c) after heating to 150 °C.

detected, was saturated with methanol at room temperature.

(iii) Using the same flow system, the experiments were repeated making use of a Barnes diffuse reflectance cell (cell III). The experiments in which TiO_2 was used as catalyst were also carried out in this cell. It appeared to be particularly suited for the recording of the gas phase in equilibrium with the working catalyst. This was accomplished by replacing the reflecting surface by a plain mirror. The reacting catalyst (0.02 g) was positioned on the mirror in such a way that it was kept out of the IR beam. In the experiments of this type, the spectra were recorded during the first minutes after the methanol vapor stream had started to flow and until after the first few minutes after this stream had been stopped.

With all the cells, it is assumed that if any of the compounds adsorbed on the catalyst and subjected to reaction conditions yield the same products as observed in the oxidation of methanol under similar conditions, it is highly likely that that compound is an intermediate of the oxidation reaction.[9]

Results: Assignment of IR Bands

Adsorption Experiments on the V_2O_5/TiO_2 Catalyst. Methanol. The spectra which are shown here are representive of the many taken, all of which showed more or less clearly the same features.

The spectrum of the monolayer catalyst before adsorption of methanol (Figure 1, spectrum a) shows bands at 3650, 3750, and 1610 cm^{-1} which are probably due to hydroxyl groups. The 3650-cm^{-1} band is due to the V–OH hydroxyl group, in good agreement with the results of Hanke et al.[10] who observed this band on a V/SiO_2 catalyst at 3665 cm^{-1}. The 3750-cm^{-1} band is probably due to Si–OH hydroxyl groups,[11,12] the Si arising from surface impurities. We assign the 1610-cm^{-1} band to the O—H bending vibration and the band at 2030 cm^{-1} to the V=O overtone stretching vibration. The latter assignment is based on the fact that V_2O_5 mixed with KBr has a normal stretching vibration at 1020 cm^{-1}, an overtone at 2040 cm^{-1}, and a weak band at 1975 cm^{-1}; the latter seems to be too
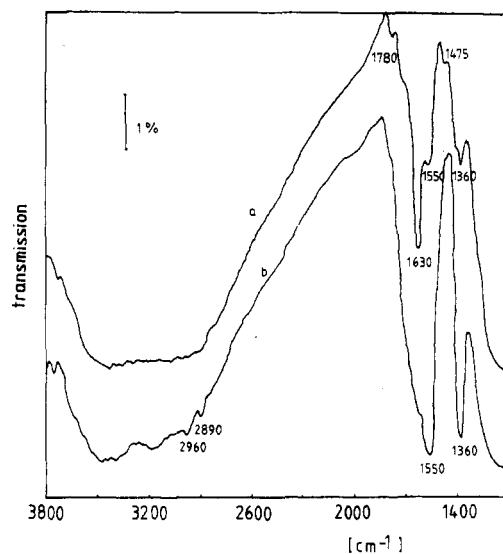
weak to be observed in the spectrum of the monolayer V_2O_5/TiO_2 catalyst and the normal stretching band was not distinguishable due to strong TiO_2 lattice vibrations.

Figure 1b shows that bands appear at 1445, 2829, and 2928 cm^{-1} when methanol is adsorbed on the catalyst; these bands can be assigned to the methoxy CH bending vibration and to symmetrical and asymmetrical CH stretching vibrations, respectively.[13] The broad band at 3400 cm^{-1} is probably due to newly formed hydroxyl groups.[11,12] It is not likely that this band is due to water since it did not disappear at higher temperatures.

When the catalyst was heated to 150 °C (Figure 1c), bands appeared at 1360 and 1550 cm^{-1}. Following Nakamoto,[14] these bands are assigned to the O–C–O symmetric stretching and the asymmetric stretching vibrations, respectively. Assuming that oxidation of methanol occurred, the 1650-cm^{-1} band was assigned to the C=O stretching vibration of adsorbed methyl formate. To support this assignment, methyl formate was adsorbed on the catalyst at the same temperature, when the same band was found; the other characteristic bands of methyl formate were difficult to observe due to overlapping adsorption bands from other species.

With increase in temperature, the C–H stretching vibration bands shifted to 2833 and 2938 cm^{-1} (Figure 1c). This shift was also observed by Chung et al.[15] who studied the methoxy C–H stretching bands on MoO_3.

At the same time, small bands appeared at 2890 and 2960 cm^{-1}; we shall give an explanation for these bands later. In the simultaneously recorded gas-phase spectrum, a band appeared at 1730 cm^{-1}; this indicates the presence in the gas of C=O bonds from either formaldehyde or methyl formate.

Formaldehyde. When the adsorption experiment was repeated with formaldehyde, the spectrum at 100 °C showed a band at 1630 cm^{-1} which we assume to be the C=O stretching vibration of adsorbed formaldehyde (Figure 2, spectrum a). The small band at 1475 cm^{-1} was assigned to a formaldehyde C—H bending vibration and

Figure 2. Infrared spectra of V_2O_5/TiO_2 recorded after adsorption of formaldehyde at room temperature and heating to (a) 100 °C and (b) successively to 180 °C.

(9) Peri, J. B. In *Catalysis*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: West Berlin, 1980; Vol 5.
(10) Hanke, Z. *Anorg. Allg. Chem.* **1978**, *438*, 176.
(11) Jackson, P.; Parfitt, G. D. *Trans. Faraday Soc.* **1971**, *67*, 2469.
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(13) Ueno, A.; Onishi, T.; Tamaru, K. *Trans. Faraday Soc.* **1971**, *67*, 3585.
(14) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978.
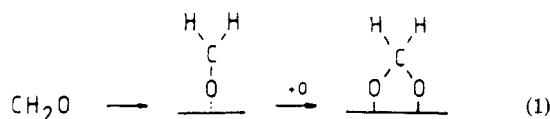(15) Chung, J. S.; Miranda, R.; Bennett, C. O. *J. Chem. Soc., Faraday Trans. 1*, in press.
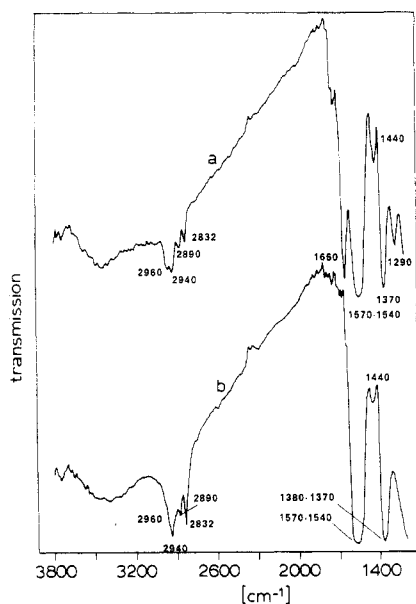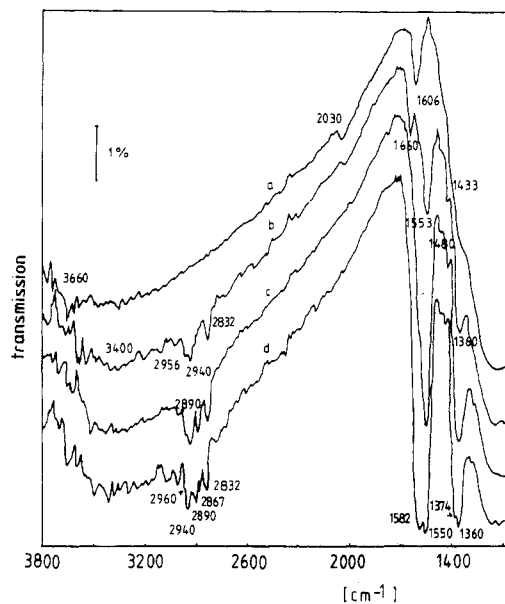
Figure 3. Infrared spectra of V_2O_5/TiO_2 recorded after adsorption at 150 °C of (a) methyl formate and (b) dimethoxymethane.

the small band at 1780 cm^{-1} was assigned to a C=O stretching vibration from formaldehyde.

The C=O band disappeared when the temperature was raised to 180 °C. New CH stretching bands appeared at 2890 and 2960 cm^{-1}, and the O—C—O stretching bands at 1360 and 1550 cm^{-1} appeared to grow in intensity. These O—C—O bands, which are also seen after adsorption of methanol, can be due either to formate or to oxymethylene. Following Greenler,[16] these bands are mostly attributed to the O—C—O stretching vibrations of formate species: for example, after adsorption of methanol on ZnO (13), bands appear at 1367, 1382, 1571, and 2870 cm^{-1} and these have been assigned to the symmetric O—C—O stretching vibration, to the C—H bending vibration, to the asymmetric O—C—O stretching vibration, and to the C—H stretching vibration of formate species, respectively. A formate species has only one C—H stretching vibration band, due to the only possible stretching vibration mode of the C—H bond; on the other hand, oxymethylene, with its two C—H bonds, might be expected to give two bands, one of which might be assigned to the symmetric and one to the asymmetric C—H stretching vibration. The bands which we found at 1360, 1550, 2890, and 2960 cm^{-1} do not correspond exactly with the characteristic formate bands. As shown in both Figure 1c and Figure 2b, we found a combination of two C–H stretching vibration bands, while the typical formate C–H stretching and bending vibrations were not found. Assuming that formaldehyde reacts with the surface as follows,

$$CH_2O \quad \longrightarrow \quad \overset{\displaystyle H \diagdown \;\diagup H}{\underset{\displaystyle \overset{|}{O}}{C}} \quad + \cdot O \quad \longrightarrow \quad \overset{\displaystyle H \diagdown \;\diagup H}{\underset{\displaystyle \overset{\diagup \;\diagdown}{O \qquad O}}{C}} \qquad (1)$$

it is more likely that the O–C–O bands which we observe are due to oxymethylene. This is consistent with the assignment of the 2960-cm^{-1} band to the C–H stretching vibration of oxymethylene, as suggested by He and Ekerdt.[6] These workers did not observe its supposed partner band at 2890 cm^{-1}, which we assign to the oxymethylene symmetric stretching vibration.

(16) Greenler, R. G. *J. Chem. Phys.* **1962**, *37*, 176.

Figure 4. Infrared spectra of V_2O_5/TiO_2 recored at 150 °C (a) before methanol vapor flows through the reactor, (b) during the first 80-s period the flow starts, (c) during the second 80-s period, and (d) during the third period of 80 s.

Methyl Formate and Dimethoxymethane. In the spectra of methyl formate and dimethoxymethane adsorbed on V_2O_5/TiO_2, the same methoxy bands 2940, 2832, and 1440 cm^{-1} and oxymethylene bands 2890, 2960, 1360, and 1550 cm^{-1} are present (Figure 3).

The previously mentioned band at 1650 cm^{-1} of adsorbed methyl formate is also observed and at 1290 cm^{-1}; there is also a band possibly from adsorbed methyl formate.

Methanol Oxidation Under Flow Conditions. Reaction over V_2O_5/TiO_2. The spectrum of the catalyst alone obtained in the flow cell shows bands at 1606, 2030, and 3660 cm^{-1}, indicating the presence of hydroxyl and V=O groups (Figure 4, spectrum a). Although Figure 4a is quite similar to Figure 1a (static cell), the hydroxyl bands in the former are more difficult to distinguish.

Figure 4b–d shows the spectra recorded while nitrogen containing about 12% methanol was passed over the V_2O_5/TiO_2 catalyst at 150 °C. Figure 4b, recorded during the first 80 s of reaction, shows methoxy bands at 1433, 2832, and 2940 cm^{-1}, O–C–O bands from oxymethylene at 1360 and 1553 cm^{-1}, an oxymethylene C–H stretching band at 2956 cm^{-1}, and a band at 1660 cm^{-1}, the latter due to adsorbed methyl formate. A broad band at about 3400 cm^{-1} is assumed to be due to hydroxyl groups.

In the simultaneously analyzed gas phase, methanol, formaldehyde, methyl formate, dimethoxymethane, and some CO all appeared to be present.

After another 80 s of reaction, the 1553- and 1360-cm^{-1} bands increased in intensity and enough oxymethylene was formed on the surface to give rise to a clear C–H stretching vibration band at 2890 cm^{-1}. The band at 1480 cm^{-1} is assigned to its C–H bend vibration (spectrum c).

In the third period of 80 s of reaction, bands appeared at 1374, 1582, and 2867 cm^{-1}; these correspond closely to bands attributed to formate species on ZnO.[13] We thus assign them to the formate C–H bending vibration, the symmetric O–C–O stretching vibration, and the C–H stretching vibration, respectively. In addition, we observe the C–H and the O–C–O bands both of oxymethylene and formate, confirming the assignments made earlier.

When a gas mixture containing 20% oxygen instead of pure nitrogen was used, a slight decrease of the bands due to all the adsorbed species, except that assigned to ad-
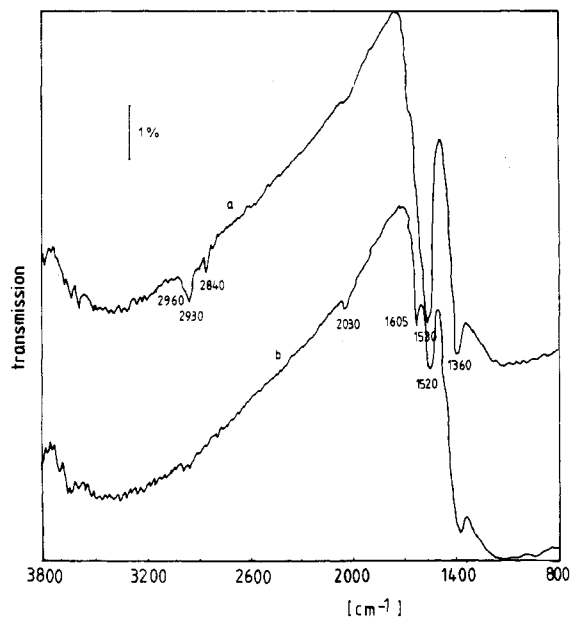
Figure 5. Infrared spectra of V_2O_5/TiO_2 recorded at 150 °C (a) 100 s and (b) 300 s after stopping the methanol vapor stream.
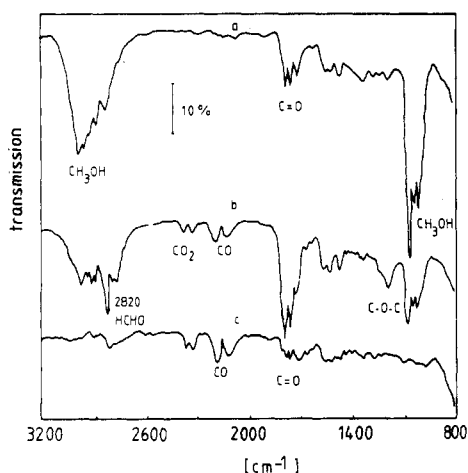

Figure 6. Infrared spectra of the gas phase just above the V_2O_5/TiO_2 catalyst surface recorded at 150 °C (a) just before stopping the methanol vapor stream and (b) 50 and (c) 100 s after stopping the gas stream.

sorbed methyl formate, was observed.

When the flow of gas was stopped, the 1580-cm^{-1} band disappeared; a shift of the asymmetric O–C–O stretching band first to 1530 cm^{-1} and then to 1520 cm^{-1} subsequently occurred (Figure 5). The C–H bands also disappeared. These changes can be explained by the formation of CO_2 to $CO_3{}^{2-}$ surface species.

As shown in Figure 6, the methanol bands corresponding to the gas-phase species decreased immediately after the gas flow was stopped, whereas the CO, formaldehyde, methyl formate, and dimethoxymethane bands still increased from about 1 min. The CO bands were still visible when the other bands had already disappeared.

Reaction over TiO_2. TiO_2 alone gives strong bands at 3650 and 3750 cm^{-1} (Figure 7, spectrum a). The positions coincide well with those observed for V_2O_5/TiO_2 (Figure 1, spectrum a), but the intensities for the material without V_2O_5 are much larger. After obtaining this spectrum, nitrogen with about 25% methanol was let into the reactor, the TiO_2 being at 150 °C. As Figure 7b shows, bands appeared at 2825 and 2930 cm^{-1} during the first minute, indicating the formation of methoxy groups. These methoxy bands are much stronger than those found on
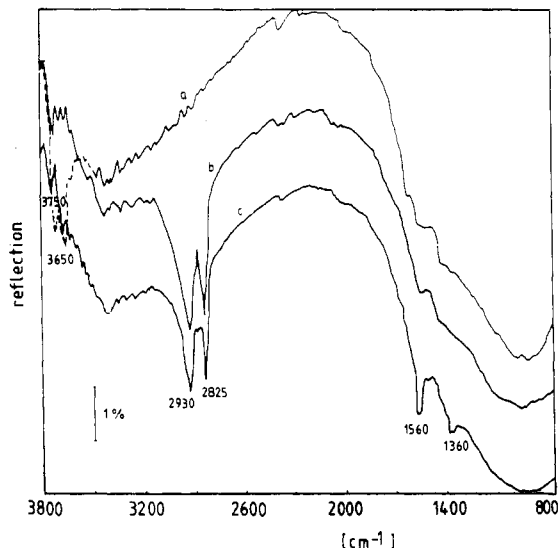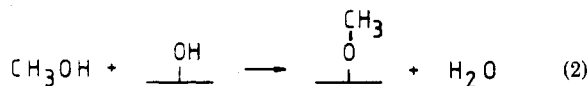

Figure 7. Infrared diffuse reflectance spectra of TiO_2 at 150 °C (a) before methanol vapor flows through the reactor, (b) 1 min after the flow started, and (c) 15 min after the flow stopped.

V_2O_5/TiO_2. The hydroxyl bands disappeared simultaneously. Some dimethyl ether and a minute quantity of CO could be detected in the gas phase. After the gas flow was stopped, the C–H bands decreased rapidly while small O–C–O bands appeared (Figure 7c).
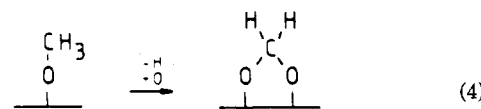
Discussion

The Reaction Mechanism. Although a number of studies of the V_2O_5 surface have been carried out,[17-20] there is little consensus of agreement on the surface structure, it being clear that V—OH and V=O species are present on the V_2O_5 surface. For the sake of clarity, in our discussion we give no detail of the surface structure of the V_2O_5 supported on TiO_2 and instead represent the surface by a straight line. We begin by discussing the surface groups present and reacting on the supported V_2O_5 and thereafter discuss those present and reacting on the clean TiO_2 support.

Reaction over V_2O_5/TiO_2. The results of the methanol adsorption experiment (Figure 1) suggest that methanol reacts with the surface, with the formation of the methoxy groups and new hydroxyl groups:

$$CH_3OH + \underset{\rule{1.2em}{0.4pt}}{\overset{OH}{\shortmid}} \longrightarrow \underset{\rule{1.2em}{0.4pt}}{\overset{CH_3}{\underset{\shortmid}{O}}} + H_2O \qquad (2)$$

$$CH_3OH \cdot \underset{\rule{1.2em}{0.4pt}}{\overset{O}{\shortparallel}} \longrightarrow \underset{\rule{1.2em}{0.4pt}}{\overset{CH_3}{\underset{\shortmid}{O}}} + \underset{\rule{1.2em}{0.4pt}}{\overset{OH}{\shortmid}} \qquad (3)$$

On heating of the catalyst, the following reaction occurs:

$$\underset{\rule{1.2em}{0.4pt}}{\overset{CH_3}{\underset{\shortmid}{O}}} \quad \xrightarrow{\overset{-H}{-O}} \quad \underset{\rule{2.5em}{0.4pt}}{\overset{\overset{H\;\;\;\;H}{\diagdown\,C\,\diagup}}{O\diagup\;\;\diagdown O}} \qquad (4)$$

This conclusion is supported by the results obtained by

(17) Haber, J. *Int. Congr. Catal., 8th, Dechema, Frankfurt am Main* **1984**, *1*, 85.
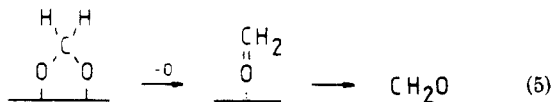
(18) Bond, G. C.; Perez Zurida, J.; Flamerz, S.; Gellings, P. J.; Bosch, H.; van Ommen, J. G.; Kip, B. J. *Appl. Catal.* **1986**, *22*, 361.

(19) Haber, J.; Kozlowska, A.; Kozlowski, R. *J. Catal.* **1986**, *102*, 52.

(20) Wachs, I. E.; Saleh, R. Y.; Shirley, S. C.; Cherrish, C. C. *Appl. Catal.* **1985**, *15*, 339.

the adsorption of formaldehyde, when reaction 4 leads to the presence of oxymethylene. The same reactions occur when methanol vapor is passed over the catalyst (Figure 4). Oxymethylene is formed and recorded during the first 80 s.
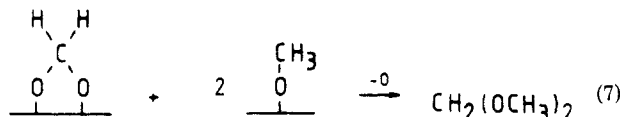
Almost immediately after methanol vapor was passed over the catalyst, adsorbed methyl formate was observed on the surface; formaldehyde, methyl formate, and dimethoxymethane were detected simultaneously in the gas phase. We suggest that formaldehyde is formed on the surface from adsorbed oxymethylene:

$$
\begin{array}{ccc}
\underset{O}{\overset{H}{\diagdown}}\underset{O}{\overset{H}{\diagup}} & \xrightarrow{-O} & \underset{O}{\overset{CH_2}{\parallel}} \\
\rule{1cm}{0.5pt} & & \rule{1cm}{0.5pt}
\end{array} \longrightarrow CH_2O \qquad (5)
$$

Methyl formate can be formed from a reaction between oxymethylene and methoxy groups on the surface:

$$ (6) $$
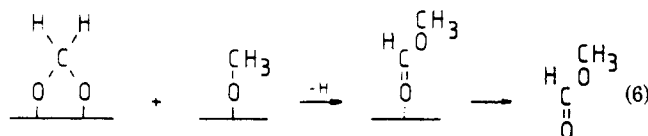
Dimethoxymethane can be formed from the same surface groups as is methyl formate:

$$
\overset{H}{\underset{O}{\diagdown}}\overset{H}{\underset{O}{\diagup}} \; + \; 2 \; \overset{CH_3}{\underset{O}{\mid}} \; \xrightarrow{-O} \; CH_2(OCH_3)_2 \qquad (7)
$$

These conclusions are supported by observations made during the adsorption of methyl formate and dimethoxymethane, respectively, on the catalyst. The same characteristic methoxy and oxymethylene bands can be observed on the surface (Figure 3).

It would appear that these reactions are slower on V_2O_5/TiO_2 than the reaction for the formation of oxymethylene since the oxymethylene concentration still grows during the formation of these products.

The surface groups desorb more easily when oxygen is present in the gas-phase; this explains the slight decrease of the IR bands when oxygen is added to the gas mixture.

After 240 s (Figure 4, spectrum d), typical formate bands appear, indicating that the conversion of oxymethylene to formate occurs:

$$ (8) $$
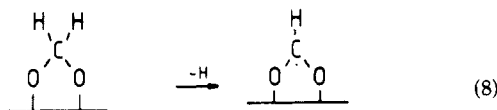
When the gas flow is stopped, this causes both an increase of the concentration of products found in the gas phase and a decrease of the concentration of surface groups. The increase of the former is explained by reactions 5-7. As time goes on, the formate groups disappear and this is followed by the disappearance of the oxymethylene groups. Reaction 8 is apparently reversible.
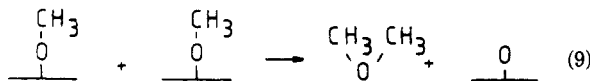
The CO_2 or CO_3^{2-} surface species disappear more slowly than the other surface species. They may be the precursors of CO; this suggestion is consistent with the slow disappearance of the CO adsorption band (Figure 6c).

Reaction on TiO_2. When methanol vapor was flowed over TiO_2, quite different results from those observed on V_2O_5/TiO_2 were obtained. Large methoxy bands appear but no O-C-O bands are observed as long as the flow goes on. The temperature at which the TiO_2 experiment is carried out is too low to give rise to methanol oxidation on the titania since almost no products could be observed. The reaction over TiO_2 must be carried out at a much

Table I

| metal ion | F | band position, cm⁻¹ | |
		theor	exptl
V^{5+}	2.4	2850–2955	
V^{4+}	1.1	2838–2945	2832–2940
Ti^{4+}	0.8	2832–2940	2825–2930

higher temperature.[5] Dimethyl ether could be formed by the combination of two methoxy groups:

$$
\overset{CH_3}{\underset{O}{\mid}} \; + \; \overset{CH_3}{\underset{O}{\mid}} \; \longrightarrow \; \underset{O}{\overset{CH_3}{\diagdown}}\overset{CH_3}{\diagup} \; + \; \underset{O}{\mid} \qquad (9)
$$

The fact that the methoxy groups are not oxidized to oxymethylene may be due to the decreased availability of oxygen on this surface. This is consistent with the lower reducibility of TiO_2 as compared to V_2O_5/TiO_2. This explanation, however, is not consistent with the fact that small O-C-O bands of oxymethylene or formate appear after stopping the vapor stream.

We offer another explanation. We suggested that the methoxy groups react on TiO_2 to give oxymethylene species and thereafter to give formate species. Under the influence of the large number of methoxy groups present on the surface, the formate groups decompose rapidly to CO. When the flow is stopped and the number of methoxy groups diminishes, the decomposition of the formate groups slows down enough to allow them to be observed. This explanation is supported by the results obtained by Yamashiti et al.,[21] who studied the methanol decomposition reaction over Cr_2O_3. They found that formate decomposes easily in the presence of surface methoxy groups to give H_2, CO, and CO_2. On V_2O_5/TiO_2, the reaction probably takes another course due to the lower concentration of methoxy groups: not enough of these groups are present to cause rapid decomposition of the formate groups.

Difference in Selectivity of the Two Materials. The present explanation hinges on the difference in reactivity of the methoxy groups on the different catalyst surfaces. Methoxy groups have been studied by Chung and Bennett[22] who observed shifts in the C-H stretching bands of these groups depending on the metal oxide on which they are chemisorbed. They compared their own results obtained on MoO_3 with literature values for the band positions of the methoxy groups on B_2O_3, GeO_3, GeO_2, SiO_2, Fe_2O_3, ZnO, Al_2O_3, MgO, and CaO and concluded that the shifts of the two methoxy bands are proportional to a function F defined as

$$ F = I_p*[(Z^2/R^3)^{3/4}]/1000 $$

in which Z is the cation charge, I_p is the ionization potential (in volts), and R is the radius (Å) of the metal ion of charge Z. The theoretical and the experimental positions of the C-H stretching vibration bands are compared in Table I for TiO_2, V_2O_5, and V_2O_4. The theoretical positions are determined by interpolation of the plot of the asymmetric and symmetric C-H stretching bands of methoxy vs the function F given by Chung and Bennett.

The theoretical positions of V^{4+} correspond closely to our experimental ones, indicating that most of the vanadium ions are in the quadrivalent state under reaction conditions.

Chung and Bennett[22] found that when methoxy chemisorbs on Mo^{6+}, which has a value of F of 2.9, it is not so

(21) Yamashiti, K.; Naito, S.; Tamura, K. *J. Catal.* **1985**, *94*, 353.
(22) Chung, J. S.; Bennett, C. O. *J. Catal.* **1985**, *92*, 173.

active for the production of formaldehyde; this is because of the weak chemisorption bond and the strong C–H bond. However, the methoxy groups formed on Mo^{5+}, which has a value of F of 1.8, produces formaldehyde owing to the moderate bond strength of the C–H bond. There is a high probability for the production of CO from the methoxy groups on Mo^{4+} because of the weakened C–H bond. In the case of other metal oxides with F greater than 1.5, the transformation of methoxy into formate at high temperature has not been observed; with the oxides with F less than 1.0, which are active for the formation of CO and CO_2, the infrared band of formate has been observed at temperatures above 150–250 °C: examples are SnO_2, Al_2O_3, Cr_2O_3, MgO, and ZnO.

For TiO_2, the value of F in the above relationship is less than 1.0 and the C–H stretching vibration frequenties of mehoxy on TiO_2 are about 10 cm^{-1} lower than the same band on V_2O_5/TiO_2. The C–H bond of methoxy on TiO_2 is thus weaker than that on V_2O_5/TiO_2, and the oxymethylene is converted more easily to formate, the precurser of CO; in contrast, the C–H bond of methoxy on V_2O_5/TiO_2 is just weak enough to form oxymethylene but also just strong enough not to oxidize immediately to formate. The bands due to methoxy species adsorbed on V_2O_5/TiO_2 are positioned in the same region of the spectrum as are the bands for the same species adsorbed on Mo^{5+}.

It can therefore be concluded that the differences in the selectivity between V_2O_5/TiO_2 and TiO_2 can be explained by the different strength of the C–H bond in the methoxy groups on the two surfaces.

A New Concept for the Theoretical Description of Solute Adsorption from Dilute Solutions on Solids[†]

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Solute adsorption from dilute solutions on heterogeneous solids containing mesopores of a large surface area and developed microporous structure is discussed. To characterize sorption properties of such adsorbents, a distribution function reflecting contributions to the global heterogeneity arising from nonuniform microporous structure and surface heterogeneity of mesopores is introduced. A suggestion to estimate these contributions from the solute adsorption data is presented.

In contrast to the theory of gas adsorption on nonporous and porous solids, theoretical description of adsorption at the liquid/solid interface is still incomplete, especially in the case of aqueous solutions and solids containing mesopores of large surface area and developed microporous structure.[1] On the other hand, adsorption from solutions on solids is one of the most important processes of utilitarian significance. It is enough to mention the numerous applications of solute adsorption from dilute aqueous solutions on activated carbons, which in the recent years have been the subject of extensive experimental studies.[2] Thus, the increasing importance of liquid/solid adsorption systems requires theoretical studies of the phenomena occurring at this interface, which facilitate control and optimization of the adsorption process.

This paper deals with the theory of solute adsorption from dilute nonelectrolytic solutions on heterogeneous solids. Thus, this description comprises also adsorption of nondissociating organic solutes from dilute aqueous solutions on activated carbons, which has a great utilitarian significance.

Generally, the energy distribution function is used to characterize the global heterogeneity of the adsorbents.[1,3-6] This distribution has a universal character because it may be used for describing adsorption on nonporous as well as microporous solids containing mesopores of large surface area and developed microporous structure.[7,8] In the case of adsorption on nonporous and wide-porous solids, this distribution provides information about surface heterogeneity, which is generally due to various atoms and functional groups exposed at the surface, imperfections and irregularities of this surface, and impurities strongly bonded with the surface. However, for ideally microporous solids (i.e., solids without mesopores) the energy distribution gives information about structural heterogeneity.

Although the energy distribution provides information about the global adsorbent heterogeneity, in the limiting cases (nonporous solids or ideally microporous solids) the source of this heterogeneity can be estimated; in the case of nonporous solids this heterogeneity may be identified with the surface heterogeneity, whereas in the case of microporous solids it is connected with the nonuniformity of their microporous structure. Therefore, for ideally

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