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Infrared Spectroscopic Studies of the Reactions of Alcohols over Group IVB Metal Oxide Catalysts

Part 2.—Methanol over TiO_2, ZrO_2 and HfO_2

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Infrared spectroscopy has been used to analyse the gas-phase reaction products, and the related adsorbed species, obtained from the decomposition of methanol over TiO_2, ZrO_2 or HfO_2 catalysts after consecutive 10 min heating periods at 50 °C intervals between room temperature and 400 °C. Somewhat different results were obtained over a 500 °C calcined TiO_2 catalyst (hydroxylated anatase surface) and an 800 °C calcined one (dehydroxylated rutile surface). The ZrO_2 and HfO_2 catalysts had dehydroxylated surfaces, were monoclinic in crystal structure, and gave products similar to those from TiO_2(800).

The principal initial surface species were several different methoxides, which were replaced by formate ions at higher temperatures. The dehydroxylated TiO_2, ZrO_2 and HfO_2 catalysts were more selective for the promotion of the dehydrogenation reaction forming methyl formate (doubtless derived from the dimerization of formaldehyde) and ultimately CO, than for the dehydration reaction forming dimethyl ether. Methoxide formation was caused by a condensation reaction with the elimination of water on the hydroxylated TiO_2 surface or by reaction with $Ti^{4+}O^{2-}$ acid–base pairs on the dehydroxylated surfaces. In all cases more than one type of methoxide species giving different ν_{C-O} absorption bands were present on a given surface. It is tentatively concluded that on ZrO_2 the methoxide group giving a band at 1163 cm^{-1}, and attributed to a monodentate methoxide co-ordinated to only one metal ion, decomposed to give the dehydrogenation products.

Both the hydroxylated and dehydroxylated TiO_2 catalysts gave rise to methane as a final product, which is clearly derived from the decomposition of the dimethyl ether. Spectroscopic evidence suggests that the reaction involves the catalytic reduction of the ether, to give the alkane plus water, by hydrogen generated by the parallel dehydrogenation reaction.

In an earlier paper[1] (Part 1) we explored the reaction pathways of propan-2-ol over a set of Group IVB metal oxide catalysts (TiO_2, ZrO_2 and HfO_2) using infrared spectroscopy. In this paper and the following one we make similar explorations for the reactions of methanol (this paper, Part 2) and ethanol (Part 3) over the same set of catalysts. We found significant and interesting differences between the results of the latter two alcohols and those obtained with propan-2-ol. As there are fewer feasible reaction pathways with methanol than with ethanol (specifically there is no simple dehydration reaction involving a single methanol molecule although, as we shall see, the bimolecular production of dimethyl ether is of interest) it is advantageous to discuss the methanol results first.

A number of previous infrared studies have explained the adsorption of methanol on the oxide catalysts Al_2O_3,[2] CeO_2,[3] CoO and Co_3O_4,[4] Cr_2O_3,[5] ThO_2,[3,6] ZnO[7,8] as well as TiO_2 [9,10] and ZrO_2 [11–14] and mixed-phase systems.[15,16] We have not encountered any such studies of methanol over HfO_2.

Experimental

Catalyst Materials

Titania (TiO_2-P25) was supplied by Degussa (FRG) with 99.5% purity. Zirconia (ZrO_2) and hafnia (HfO_2) were high-purity (99.9%) products from Aldrich Chemical Co., U.K. As described previously[1] each of these was calcined at a number of temperatures between 300 and 1000 °C for 5 h. For convenience, the different calcination products are designated in the text by the chemical symbol of the oxide followed by the calcination temperature (°C) in parentheses. Thus TiO_2(300) indicates titania calcined for the standard 5 h at 300 °C. The various catalyst samples have previously been subjected to physical characterisation studies by means of IR spectroscopy, X-ray diffractometry, and N_2 and pyridine adsorption, as also described and discussed in Part 1.[1]

The TiO_2(500) catalyst has largely hydroxylated surfaces of high specific area (77.3 m^2 g^{-1}) and the anatase crystal structure, whereas the high-temperature calcinated TiO_2(800) (14.3 m^2 g^{-1}) has the rutile structure and is strongly dehydroxylated. The variously calcined ZrO_2 (10–1.7 m^2 g^{-1}) and HfO_2 (12.5–4.3 m^2 g^{-1}) samples (300–1000 °C) also have strongly dehydroxylated surfaces of low specific areas, and are of monoclinic crystal structure. Infrared spectra from adsorbed pyridine show that all the catalysts expose increasing proportions of Lewis-acid sites on high-temperature calcination.

Infrared Spectroscopy

Infrared spectra of gas-phase and surface species were obtained with 4 cm^{-1} resolution between 4000 and 600 cm^{-1}, using a Digilab FTS 20V Fourier-transform spectrometer. The data-acquisition system allowed spectra of the adsorbed species alone to be obtained by transmission-ratioing, or absorbance subtraction, of the oxide-background and gas-phase spectra.

Self-supporting, but porous, thin wafers (*ca.* 20 mg cm^2) of the catalysts were prepared[1] and mounted inside an all-Pyrex glass IR cell equipped with NaCl windows, similar to that described by Peri and Hannan.[17] A standard procedure was

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† Part 1: G. A. M. Hussein, N. Sheppard, M. I. Zaki and R. B. Fahim, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1723.

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used for pre-cleaning the wafer in flowing O_2 ($50\ cm^3\ min^{-1}$ at 400 °C for 1 h followed by room-temperature evacuation to *ca.* 5×10^{-5} Torr†) and for obtaining spectra before and after exposing the catalyst to an equilibrium pressure of 10 Torr of alcohol. Reactions were allowed to occur in the closed cell, consecutively for a given methanol dose, at a series of stated temperatures, for a period of 10 min in each case. The spectra of the gas phase and of the adsorbed species were recorded following each reaction period after the cell had been cooled to room temperature.

Reagents, Reference Compounds and Gases

Methanol and formic acid were spectroscopic-grade BDH products subjected, prior to an experiment, to degassing by freeze–pump–thaw cycles performed under vacuum. The gases CH_4, CO_2 and CO used for spectroscopic calibration purposes were supplied by British Oxygen in high purity (99.99%).

Results and Discussion

Gas-phase Spectra

All spectra were measured at room temperature after successive treatments of the methanol–catalyst system at different temperatures in a closed cell at the various temperatures indicated.

Methanol over TiO_2(500)

Fig. 1(*a*)–(*c*) show that between room temperature and 250 °C methanol predominates in the gas phase, as shown by the ν_{OH} and ν_{C-O} absorptions at 3680 and 1035 cm^{-1}, respectively. In Fig. 1(*c*) a trace of dimethyl ether (ν_{C-O} at 1180 cm^{-1}) and a small amount of carbon monoxide (2143 cm^{-1}) is also present. After treatment at 300 °C [Fig. 1(*d*)] a major fraction of methanol has reacted and dimethyl ether absorptions (1180, 1100 and 930 cm^{-1}) are greatly increased in intensity. Enhanced, but still weak, absorption from CO is present and a trace of methane can also be identified (3018 and 1307 cm^{-1}). After heating at 350 °C [Fig. 1(*e*)] all the methanol has decomposed, the dimethyl ether absorption has passed its peak of intensity and large amounts of methane have been produced. An increased amount of CO is accompanied by some gas-phase CO_2 (2350 and 667 cm^{-1}). After reaction at 400 °C [Fig. 1(*f*)] all the dimethyl ether has decomposed in turn and only methane, CO and CO_2 are apparent in the gas phase in the approximate ratios of 4 : 4 : 1 on the evidence of their infrared absorption bands. Hydrogen is very likely to be an additional product but this has no infrared-active absorption band. Over the range 250–400 °C complex changes in the *ca.* 3000 cm^{-1} ν_{CH} region of the spectrum occur as the clear-cut reaction sequence $CH_3OH \rightarrow CH_3OCH_3 \rightarrow CH_4$ progresses from reagent to final product. Possible reaction pathways are discussed below.

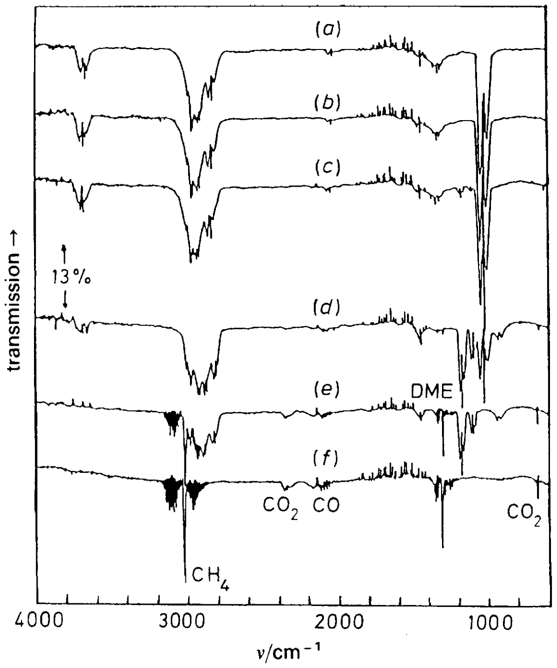

Fig. 1 Room-temperature IR spectra of the gaseous products from the reaction of an equilibrium pressure of 10 Torr methanol over the TiO_2(300) catalyst, each taken after allowing the alcohol to interact successively with the catalyst in a closed cell for 10 min intervals at (*a*) room temperature, (*b*) 200, (*c*) 250, (*d*) 300, (*e*) 350 and (*f*) 400 °C. DME, dimethyl ether

Methanol TiO_2(800)

The gas-phase infrared spectra (Fig. 2) show qualitatively that the same gas-phase products are produced as over TiO_2(500) although to a reduced degree after any given temperature of the reaction sequence. In addition, small amounts of methyl formate ($\nu_{C=O}$ at 1740 cm^{-1}) first appear at 250 °C, reach a maximum after 300 °C and then decline again. This product is most probably produced by dimerization of the first dehydrogenation product, formaldehyde, as $2H_2C{=}O \rightarrow (HCO)OCH_3$. The dimethyl ether reaches its peak after 350 °C and, together with residual methanol, remains in a smaller quantity after 400 °C. The amounts of the final gas-phase species after 400 °C are in the approximate ratios of methane : CO : CO_2 : ether : methanol of 5 : 6 : 3 : 1 : 1.

The production of more of the carbonyl-containing product (in this case methyl formate) in the intermediate

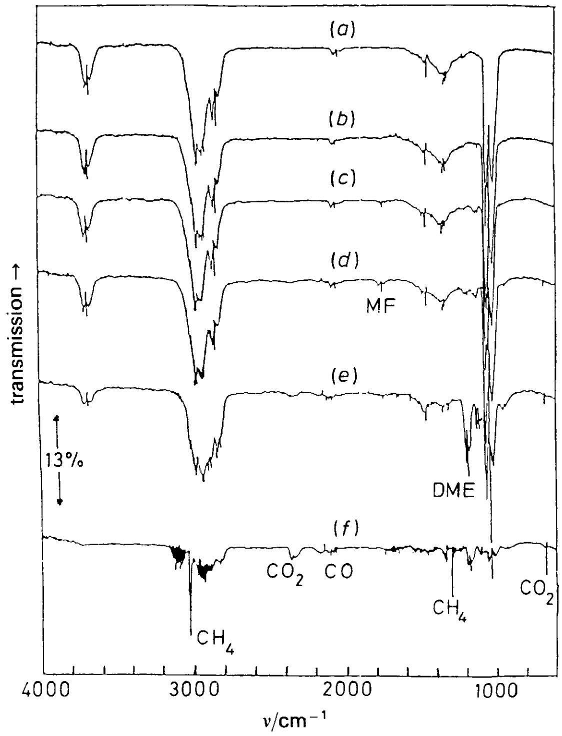

Fig. 2 As for Fig. 1 but for methanol over the TiO_2(800) catalyst; MF, methyl formate

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† 1 Torr = 101 325/760 Pa.

stages, and the reduced rate of overall alcohol decomposition over TiO_2(800) compared with that over TiO_2(500), reflect earlier findings from propan-2-ol decomposition over the same catalysts.[1] However, in the latter case neither the intermediate ether dehydration product (from propanol, only the easily accessible final monomolecular dehydration product, propene, occurred) nor an alkane final product (propane rather than methane) were obtained.

Methanol over ZrO_2(500) *and* HfO_2(500)

Over ZrO_2(500) only a minor fraction of methanol decomposes, even after the final heating at 400 °C. The principal products are CO and CO_2, both of them present in similar final amounts as for the reactions over TiO_2(500) or TiO_2(800). HfO_2(500) additionally gives rise to methyl formate, still in a small quantity but in a greater amount than over TiO_2(800). Its concentration peaks after heating at 300 °C. After 400 °C, small amounts of dimethyl ether and methane appear in addition to methanol and the product CO. After 300 °C, CO_2 is produced in a much greater quantity than over the other catalysts. He and Ekerdt[11] reported CO, H_2 and CH_4 as main products from methanol over another ZrO_2 catalyst taken up to 500 °C. CO_2 and H_2O were additionally reported at lower temperatures.

Spectra from Adsorbed Species

Infrared spectra of the adsorbed species were obtained, in addition to those from the gas phase, after each temperature stage of reaction. They were also all measured at room temperature and the spectra were obtained free of gas-phase contributions by ratioing against the spectra of the latter. In a few significant cases the background spectra of the catalysts before reaction were also ratioed out. The spectra are illustrated in the chemically significant regions 3800–2400 cm^{-1} (ν_{OH} and ν_{CH}) and 1800–1000 cm^{-1} ($\nu_{C=O}$, δ_{CH} *etc.*).

Methanol and Products adsorbed on TiO_2(500)

The spectra are shown in Fig. 3. Fig. 3(*a*) is that of the hydroxylated TiO_2 surface prior to the addition of methanol. It shows the usual multiple ν_{OH} absorptions (3720, 3665 and 3640 cm^{-1}) of anatase,[1,18] together with a strong lattice absorption increasing to lower wavenumbers. The adsorption of methanol at room temperature [Fig. 3(*b*)] leads to a very broad absorption region between *ca.* 3500 and 2600 cm^{-1} which denotes the presence of a large concentration of hydrogen-bonded OH groups. Some of these may be from surface OH groups hydrogen-bonded to adsorbed methanol molecules; others will be from methanol molecules hydrogen-bonded either to surface oxide ions or to other adsorbed methanol molecules. Relatively broad ν_{CH_3} absorptions [compared with the spectra on TiO_2(800), discussed below] at 2950–2920 and 2840–2810 cm^{-1} show the presence of a mixture of surface methoxide species, CH_3O^-, and adsorbed intact methanol molecules.[9] The presence of the latter is clearly shown by the occurrence of a broad δ_{OH} absorption, superimposed on expected $\delta_{CH_3,as}$ and $\delta_{CH_3,s}$ absorptions in the 1450–1380 cm^{-1} region. This region of the spectrum is mostly clearly illustrated in Fig. 5 after further ratioing with the TiO_2 spectrum. A broad absorption at *ca.* 1630 cm^{-1} clearly arises from the δ_{HOH} mode of adsorbed water molecules.[1] These will have been formed by the subsequent reaction of methanol with the hydroxylated surface[1]

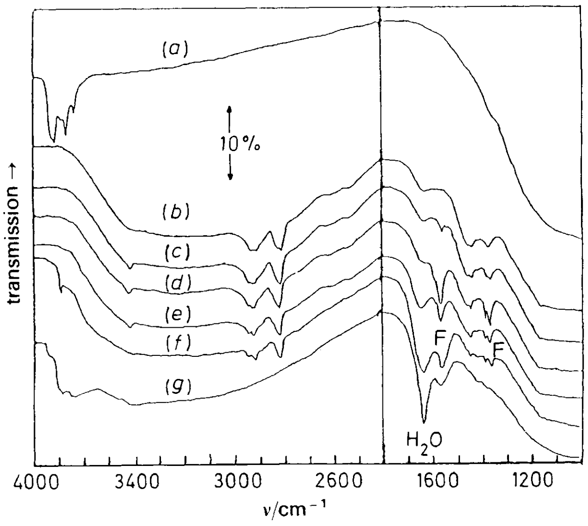

Fig. 3 Room-temperature IR spectra of the adsorbed species plus oxide background from methanol over TiO_2(300) after the corresponding stages of reaction to those given in Fig. 1 at (*b*) room temperature, (*c*) 200, (*d*) 250, (*e*) 300, (*f*) 350 and (*g*) 400 °C. All spectra have been ratioed against those of the gas-phase products (Fig. 1). (*a*) is the spectrum of the oxide before the introduction of methanol. F, surface formate

$$CH_3OH + OH^-(s) \rightarrow CH_3O^-(s) + H_2O \qquad (1)$$

where (s) denotes a species bonded to the surface.

We shall, in general formulate surface reactions in terms of ionic rather than the [illegible]ive covalent surface species; the reality will be somew[illegible]etween these two extremes. A negatively charged species will be assumed to be co-ordinated to a metal ion. In the case of H^-(s), what actually happens is more probably covalent bonding to Ti^{4+}, Zr^{4+} or Hf^{4+} to give an HTi^{3+} species *etc.*, exploiting the variable valency of the transition metal.

Methoxide species can also be formed by reaction with surface O^{2-} on dehydroxylated parts of the surface by the reaction:

$$CH_3OH + O^{2-}(s) \rightarrow CH_3O^-(s) + OH^-(s) \qquad (2)$$

After heating at 200 °C [Fig. 3(*c*)] a weak but sharp absorption at 3420 cm^{-1}, also observed in the reaction of propan-2-ol,[1] shows that a new surface OH^--containing species has been formed, probably by reaction (2). As noted previously,[1,19] its sharp profile shows a lack of involvement in hydrogen bonding; perhaps it is a sub-surface hydroxide ion. The absorption is not strong and so the reaction is probably limited to a few special surface sites on a small proportion of the surface.[19,20]

The surface methoxide species formed by reactions (1) and (2) are likely to be intermediates in the formation of the gas-phase product dimethyl ether *via* the surface reaction

$$2CH_3O^-(s) \rightarrow CH_3OCH_3\uparrow + O^{2-}(s) \qquad (3)$$

Also after 200 °C, a new sharp absorption occurs at 1560 cm^{-1} and denotes the initial production of surface formate species, very probably formed by oxidation of a transient formaldehyde intermediate, according to the reaction

$$H_2C{=}O(s) + OH^-(s) \rightarrow H_2\uparrow + HCOO^-(s) \qquad (4)$$

The amount of surface formate is much enhanced after 250 °C but is reduced again after higher temperatures. Such species are known to decompose to gas-phase CO by the reaction:

$$HCOO^-(s) \rightarrow CO\uparrow + OH^-(s) \qquad (5)$$

and also to some CO_2, possibly by the alternative reaction:

$$HCOO^-(s) \rightarrow CO_2\uparrow + H^-(s) \qquad (6)$$

The overall catalytic reactions, to which reactions (4)–(6) contribute, are reviewed at the end of Part 3.

The amounts of CO and CO_2 increase over the temperature range during which surface formate is consumed, in agreement with the requirements of eqn. (7) and (8). In addition to the strongest absorption of the formate ion at 1560 cm^{-1} ($\nu_{CO_2^-, as}$), other well known companion bands occur at 1385 (δ_{CH}) and 1365 cm^{-1} ($\nu_{CO_2^-, s}$) and are clearly apparent after 250 °C.

With increasing temperatures the strengths of the ν_{CH} absorptions from methoxide *etc.* gradually decline, until after 400 °C they have completely disappeared. This is the same temperature after which even dimethyl ether disappears from the gas phase (Fig. 2) and methane becomes the dominant CH-containing species.

The water absorption band at 1630 cm^{-1} continues to increase in intensity throughout, doubtless because the bimolecular dehydration of methanol to dimethyl ether continues to generate H_2O at the higher temperatures. After 400 °C, the only other surface species present is a residual amount of formate. The further enhancement of the 1630 cm^{-1} band between 350 and 400 °C, when methanol is no longer present for dehydration to the ether, suggests that the generation of methane by final reaction of the ether is also accompanied by water formation.

This last observation implies that the overall final gas-phase reaction is probably $CH_3OCH_3 + 2H_2 \rightarrow 2CH_4 + H_2O$, presumably with surface methoxide species again playing a role as an intermediate at the higher temperature; perhaps in the reactions

$$CH_3OCH_3 + O^{2-}(s) \rightarrow 2CH_3O^- \quad (7)$$

$$2CH_3O^-(s) + 2H_2 \rightarrow 2CH_4 + H_2O + O^{2-}(s) \quad (8)$$

As each dehydrogenation of methanol to CO generates two hydrogen molecules, the requirement for complete reduction of the ether to methane is that at least half as many surface-catalysed dehydrogenations to CO should occur as the number of methane molecules produced. This is consistent with the above-mentioned finding that CH_4 and CO are present in approximately equimolecular amounts in the final products. Equally, two methane molecules should be produced per ether molecule decomposed according to eqn. (7) and (8). This seems approximately to be the case from analysis of the gas-phase spectra. However, a more accurate assessment is not possible because the concentration of the ether varies rapidly between temperature steps so that the maximum amount of ether produced cannot be determined.

Methanol and Products adsorbed on TiO_2(800)

The spectra are shown in Fig. 4. The background spectrum from the oxide alone [Fig. 4(*a*)] shows, as before,[1] that few surface OH^- ions are retained after the higher-temperature calcination involving the conversion of anatase to rutile.

The absorption of methanol at room temperature [Fig. 4(*b*)] again shows a broad ν_{OH} absorption from hydrogen-bonded OH groups but this is much weaker than is the case for TiO_2(500), as expected from the inability of reaction (1) to take place. Also the ν_{CH} and δ_{OH} regions suggest the presence of both surface methoxide and undissociated methanol. However, after 200 °C the ν_{CH} absorptions have substantially sharpened implying the presence mainly of methoxide ions. In addition, the broad ν_{OH} absorption has been replaced by the sharper band at 3420 cm^{-1} which is known to be characteristic of rutile surfaces.[19,20] The band, probably produced by reaction (2), is considerably stronger than in the TiO_2(500) case implying the presence of a greater proportion of the, probably Lewis, reactive sites which give rise to this species.

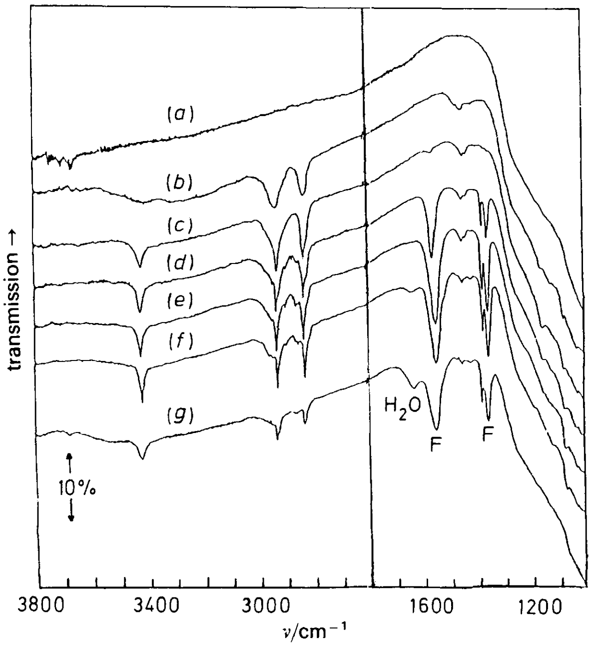

Fig. 4 As for Fig. 3 but for the adsorbed species from methanol over the TiO_2(800) catalyst

The much reduced presence of methanol molecules on the surface, despite only a slight reduction in the amount of gas-phase methanol present, implies that reaction (2) has occurred at the sites that were available for adsorption of intact methanol before heating to 200 °C.

After 250 °C, clear-cut formate absorptions appear at 1560, 1385 and 1365 cm^{-1}. These grow in strength until after 300 °C when they decline in intensity once again. However, after 400 °C they remain in much greater quantity than for the TiO_2(500) case, even though the amount of gas-phase CO is, if anything, greater. As the formate is presumed to be derived from a formaldehyde intermediate, this again shows that TiO_2(800) is a better dehydrogenation catalyst.

Because of the lack of surface OH^-, water cannot be generated by reaction (1) and so it is not until the dehydration reaction of methanol to dimethyl ether sets in after 350 °C that appreciable water absorptions are observed at 1630 cm^{-1}. Residual methoxide absorptions, even after 400 °C, parallel the continued presence of methanol and the ether in the gas phase at this stage over TiO_2(800).

Methanol and Products adsorbed on ZrO_2(500) *and* HfO_2(500)

Owing to considerable scattering of radiation by these low-area catalyst discs, the spectra of the adsorbed species were of poor quality. Hence only a few of these, ratioed against the oxide background, are shown together with, for comparison purposes, analogous spectra from TiO_2(500) and TiO_2(800).

Fig. 5 compares the spectra obtained on the four oxide surfaces after adsorption of methanol at room temperature. The principal additional interest of these spectra relates to the different patterns of absorption bands that occur between 1250 and 1000 cm^{-1} and arise from the ν_{C-O} modes of methoxy groups. It seems now that absorptions at the higher wavenumbers of this region (> 1100 cm^{-1}) are probably associated with methoxy ions that are monodentate, *i.e.* bonded to single-metal ions, whereas those at < 1100 cm^{-1} are associated with bi- (or poly-) dentate ions that are coordinated to more than one metal ion.[3,6,14,18] These different species can have different reactivities; see also ref. 16.

It is seen that in these terms there are notable differences between the four oxide samples. Thus TiO_2(500) and

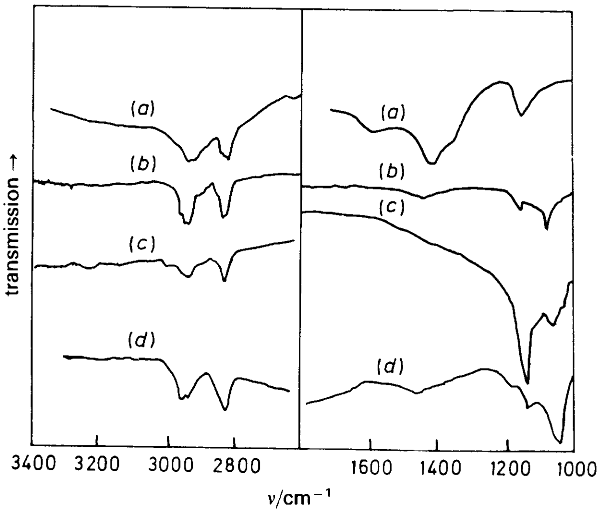

Fig. 5 Infrared spectra of the species adsorbed from methanol at room temperature after further ratioing against the spectra of the clean oxide discs: (*a*) TiO_2(300); (*b*) TiO_2(800); (*c*) ZrO_2(500) and (*d*) HfO_2(500)

ZrO_2(500) with strong ν_{C-O} absorptions at 1160 and 1163 cm^{-1}, respectively, seem to have predominantly monodentate methoxide species, whereas TiO_2(800) and HfO_2(500), with stronger absorptions at *ca.* 1080 and 1100 cm^{-1}, respectively, have predominantly bidentate species. These ν_{C-O} absorptions are particularly strong with ZrO_2 and in that case provide an indication that it is the monodentate species that reacts at the lower temperature, *i.e.* after 250–300 °C, under circumstances when the only gas-phase product is CO from dehydrogenation. A more detailed study of the changes in such absorption bands in relation to gas-phase products would repay effort. Weaker absorptions on TiO_2(800), ZrO_2(500) and HfO_2(500) occur at *ca.* 1160, 1058 and 1195 cm^{-1}, respectively. The ν_{C-O} absorptions for ZrO_2 are similar in position and relative intensity to those reported previously.[14] In that case, ^{18}O isotopic substitution was used to show that it is the OH bond of methanol, rather than the C—O bond, that is broken on methoxide formation, as in eqn. (2).

Conclusion

By comparison with the previously studied reaction of propan-2-ol over these same catalysts, the unexpected result in the present study was the production of the alkane CH_4 as a principal product. Others have previously noted methane as a product of the reaction of methanol over oxides.[5,9,11] Several of these authors also observed dimethyl ether as well as methane amongst the products. Our work seems to establish the ether firmly as the source of the methane. We shall show in Part 3 that ethane is likewise produced from diethyl ether as an intermediate product over TiO_2(500). It has also been found that over tungstophosphate catalysts more alkanes are produced from alcohols, the more the ether intermediate is adsorbed.[21] Our suggested explanation of the origin of the alkane implies that parallel dehydrogenation and dehydration reactions are necessary, with the dehydrogenation producing the necessary hydrogen. If this conclusion is correct, the final proportions of methane obtained over different oxide catalysts may be related to their different efficiencies as dehydrogenation catalysts.

Carrizosa *et al.*[9] earlier made the alternative suggestion that methane produced from methanol over rutile, and (unlike our results) ethane produced over anatase, are generated by the reaction of surface CH_3—Ti groups. As evidence for the latter, they cited the observation of two ν_{CH_3} absorptions at 2970 and 2860 cm^{-1}, obtained from methanol adsorption after prolonged heating at 370 °C. However, these assignments seem unlikely in view of the fact that authentic compounds containing such groups have a different pattern of absorptions at *ca.* 2950 (s, bd), 2880 (s) and 2800 (m) cm^{-1}.[22] Fig. 4(*d*)–(*f*) show analogous absorptions to those cited by Carrizosa *et al.* at *ca.* 2960 and 2865 cm^{-1}, but these are from the adsorbed formate ions.

The central role of methoxide surface intermediates, which are present under all circumstances until the reaction is complete (Fig. 3 and 4), is apparent throughout. This important point is elaborated further in the discussion of the overall results from the three alcohols in Part 3.

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References

1 G. A. M. Hussein, N. Sheppard, M. I. Zaki and R. B. Fahim, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1723.
2 R. G. Greenler, *J. Chem. Phys.*, 1962, **37**, 9, 209.
3 J. Lamotte, V. Moravek, M. Bensitel and J-C. Lavalley, *React. Kinet. Catal. Lett.*, 1988, **36**, 113.
4 G. Busca, R. Guidetti and V. Lorenzelli, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 989.
5 K. Yamashita, S. Naito and K. Tamaru, *J. Catal.*, 1985, **94**, 3585.
6 X. Montague, J. Lynch, E. Freund, J. Lamotte and J-C. Lavalley, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 1417.
7 A. Ueno, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, 1971, **67**, 353.
8 M. Nagao and T. Morimoto, *J. Phys. Chem.*, 1980, **84**, 2054.
9 I. Carrizosa, S. Castaner and G. Munuera, *J. Catal.*, 1977, **49**, 265.
10 Y. Suda, Y. Morimoto and M. Nagao, *Langmuir*, 1987, **3**, 99.
11 M-Y. He and J. G. Ekerdt, *J. Catal.*, 1984, **87**, 239.
12 Y. Nakano, I. Izuka, H. Hattori and K. Tanabe, *J. Catal.*, 1979, **57**, 1.
13 T. Y. Yamaguchi, Y. Nakano and K. Tanabe, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2482.
14 M. Bensitel, V. Moravek, J. Lamotte, O. Sauer and J-C. Lavalley, *Spectrochim. Acta, Part A*, 1987, **43**, 1487.
15 F. S. Feil, J. G. van Ommen and J. R. H. Ross, *Langmuir*, 1987, **3**, 668.
16 W. E. Farneth, R. H. Staley, P. J. Dormaille and R. D. Farlee, *J. Am. Chem. Soc.*, 1987, **109**, 4018.
17 J. B. Peri and R. B. Hannan, *J. Phys. Chem.*, 1960, **64**, 1526.
18 A. A. Tsyganenko and V. N. Filimonov, *J. Mol. Struct.*, 1973, **19**, 579.
19 J. Graham, C. H. Rochester and R. Rudham, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2735.
20 P. Jones and J. A. Hockey, *Trans. Faraday Soc.*, 1971, **67**, 2669; 2679.
21 T. Hibi, K. Takahashi, T. Okuhara, M. Misono and Y. Yoneda, *Appl. Catal.*, 1986, **24**, 69.
22 G. P. McQuillan, D. C. McKean and I. Torto, *J. Organomet. Chem.*, 1986, **312**, 183.

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